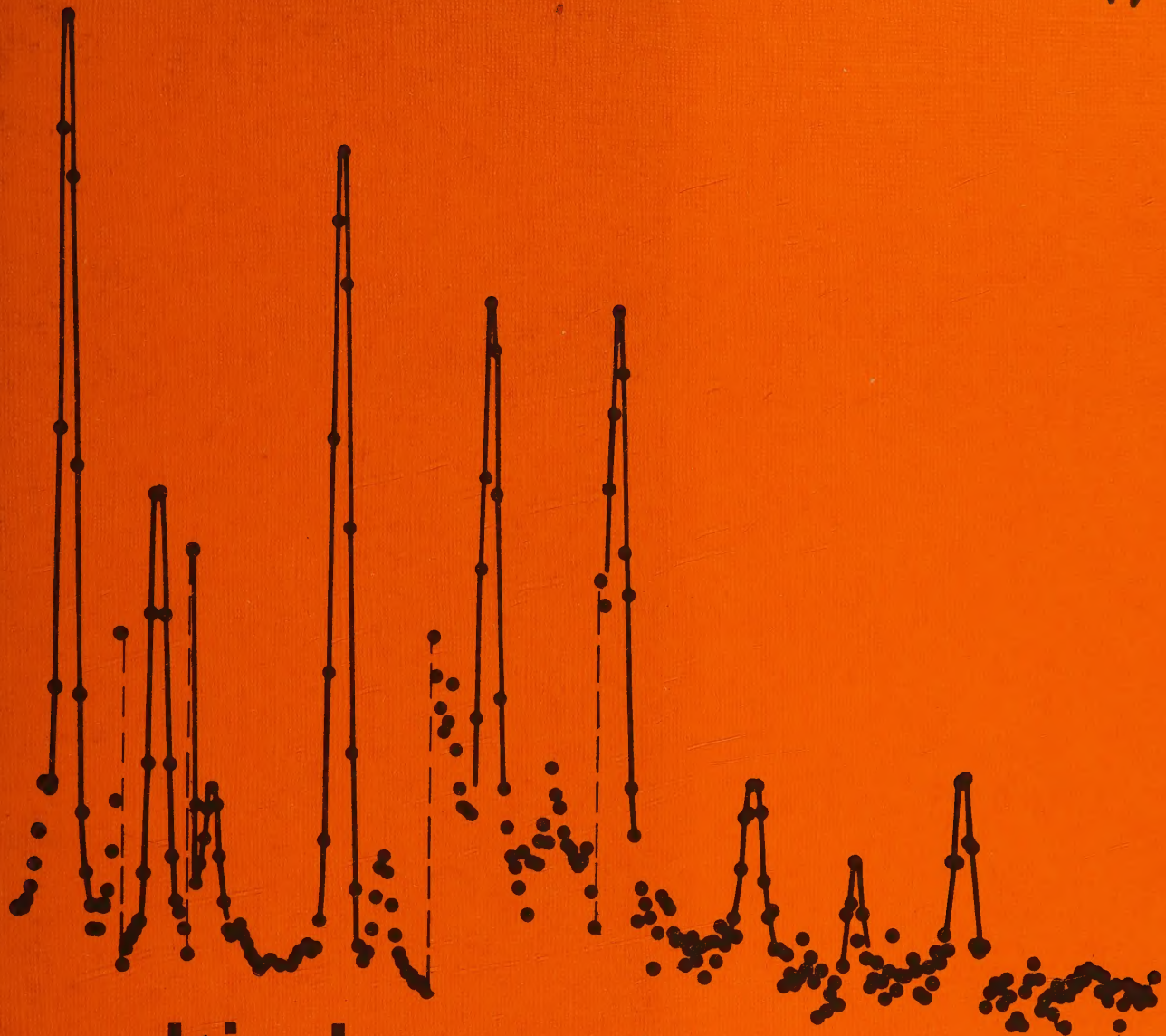


Rund 1974



multi-element trace analysis by proton induced x-ray emission

Thomas B. Johansson

MULTIELEMENT TRACE ANALYSIS BY PROTON INDUCED X-RAX EMISSION

av

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to Lena

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by

Thomas B. Johansson

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SUMMARY

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INTRODUCTION

Growing concern about the negative consequences of man's activities has stimulated interest in the role and significance of natural and pollution trace elements in the environment. Also, in science, medicine and technical development, trace elements are often of fundamental importance. Systematic investigations of related questions require analytical methods capable of rapid, low-cost multi-element analysis of many samples.

The present work introduces trace element analysis by X-ray emission employing the new combination of protons in the MeV range to excite and solid-state detectors to record the characteristic X-rays. Various aspects of the method and the physics underlying it are evaluated. The determination of up to 14 elements in aerosol size fractions in a model study of a natural atmosphere is presented as an example of its application.

The technique of X-ray emission analysis is well established and has found many routine applications. The basic principle is well-known: When a vacancy in an inner shell of an atom is filled by an electron, electromagnetic radiation or an Auger electron is emitted. This radiation (X-ray) is characteristic of the atom and by determining its energy qualitative analysis can be performed. By creating inner shell vacancies in a controlled way and recording the intensity of a certain X-ray line, quantitative analysis can be performed.

Generally, inner shell vacancies are produced in the atoms of a sample by irradiation with X-rays or electrons. Intense background radiation from scattered X-rays or bremsstrahlung limits the sensitivity. Also, in the X-ray case, very intense fluxes of suitable exciting radiation are not available. Ions, on the other hand, give rise to very low bremsstrahlung backgrounds. Thus, low energy protons have been used for surface studies. As the X-ray production cross section increases rapidly with proton energy at low energies, the sensitivity of the analysis can be improved by employing increasing beam energies until the signal/background ratio reaches a maximum.

X-ray detection has generally been based on wave-length dispersion in crystals, offering high resolution capability for the X-ray line selected.

With the advent of lithium-drifted solid state detectors, capable of resolving characteristic lines from adjacent elements, X-ray quanta from many elements in a sample can be recorded simultaneously, efficiently and conveniently.

PROTON-INDUCED X-RAY EMISSION ANALYSIS

Multi-element trace analysis employing MeV protons as an excitation source and a Si(Li)-detector to record the characteristic X-rays is introduced in paper I. Interference-free detection limits in thin samples are indicated to reach into the 10^{-12} g range. As an example, 11 elements were determined in an aerosol sample. The technique: Proton-Induced X-ray Emission - PIXE - is further developed and applied in the following papers. In principle, all elements can be determined by PIXE. A practical limitation is the X-ray attenuation in the sample which, for low Z elements, restricts the possibilities of quantitative analysis. For practical samples, K-radiation is convenient for quantitative analysis of elements with Z between, roughly, 15 and 50 while L-radiation generally offers better sensitivity for higher Z elements at the same proton energy. Lighter elements are qualitatively detected in PIXE analysis and can be determined quantitatively under favourable circumstances.

The more interesting properties of PIXE include the following:

1. The detection limit is low because:
 - a) intense fluxes of exciting radiation are readily available,
 - b) X-ray production cross sections for particles with energies in the MeV range are large and
 - c) the background associated with the exciting radiation is low.
2. The detection limit shows only modest variation with Z of the element.
3. Many elements (with $Z \geq 15$) can be determined simultaneously in a quantitative manner by utilizing a semiconductor detector coupled to a multichannel analyzer or a small computer.
4. The procedure requires little time, especially when compared to single-element analytical methods.
5. Only standard equipment in a small accelerator laboratory is required for an analytical program.
6. The information obtained is not dependent on the chemical state of the

detected elements.

7. Only small and thin samples can be analyzed.

DETECTION LIMITS

For an estimate of the detection limits, 100 counts in a peak was chosen as the detection criterion. In paper III the lower limit of detection was then calculated as function of Z of the target atom using experimental X-ray production cross sections. In an actual situation conditions vary with sample type and composition. In paper V, in which a specific analytical problem is considered, detection limits are presented for that particular situation.

The lower limit of detection depends on several parameters. In the case of analysis restricted by the maximum possible count-rate with the electronics available, the sensitivity is limited by the efficiency with which we can make use of the counting apparatus. By using suitable absorbers, the large low energy background contribution to the total counting rate can be significantly reduced, in contrast to the situation when X-rays are used for excitation and a large fraction of the total number of counts originate in the scattering of exciting radiation. The interference-free lower limit of detection is ultimately determined by the analysing time available. This mode of operation is possible if the target can withstand sufficient beam intensity when the best available counting geometry is used. The intensity needed is then a function of sample size, X-ray and background production cross sections. To optimize detection limits for certain elements we can choose a suitable combination of beam energy and absorbers. Further limitations may arise from the composition of the sample, as in some cases the energy difference between X-ray lines from different elements are not sufficient to allow interference-free analysis. Other limitations may, of course also arise from impurities in the backing material. In paper III examples of analytical problems where PIXE may be employed are given. They include the analysis of aerosol size fractions, oil slick identification by a finger-print approach and the analysis of water and blood serum.

The ideal task for PIXE is the determination of 10-15 elements present in amounts between 10^{-8} and 10^{-11} g in many small samples which can be applied to supporting foils on an area of the order of a uniform accelerator beam, $\lesssim 1 \text{ cm}^2$. PIXE is advantageous especially if only a very minute amount of the sample is available or large samples are very expensive to obtain. There are many situations in which this is the case. With a small sample we here mean a mass/area concentration that gives little problems with X-ray absorption or proton energy loss in the sample. This, of course, can be more easily dealt with in the case of a homogeneous target.

BEAM HOMOGENEITY

Quantitative PIXE-analysis of nonhomogeneous samples can be performed if the flux of ionizing radiation in the beam is uniform, cf. paper III. A uniform beam can be obtained by the electronic sweeping of a collimated beam as demonstrated in paper III or by inserting a diffuser foil as used in paper V. The diffuser foil approach has the advantage of providing a beam intensity that is uniform also in time which makes dead-time corrections simple, but 90-95 % of the original beam intensity is lost on the defining collimators. In both cases, knowledge about the beam profile is required. This information can be obtained by determining the X-ray intensity from a small probe of suitable material as a function of its position in the beam as described in paper II. Although relatively timeconsuming, this method permits very good geometrical resolution and is applicable to all accelerator beams of charged particles.

X-RAY PRODUCTION CROSS SECTIONS

Quantitative PIXE-analysis is generally performed by direct calculation of the results from physical constants and a few parameters determined for each irradiation. Standard samples are used only to check the stability of the system. This approach has clear advantages when heterogeneous samples are used and when analysing conditions are frequently changed. A fundamental parameter is the X-ray production cross section

$$\sigma_p = \sigma_{\text{ion}} \omega k$$

where ω is the fluorescence yield and k the relative intensity of the X-ray line considered, i.e. the ratio between K_{α} and the total K intensity. Values of ω and k are available¹⁾. Theoretical expressions for inner shell ionization cross sections, σ_{ion} , based on plane wave Born approximation²⁾ (PWBA) or binary encounter³⁾ (BEA) calculations are available. Although extensive at low proton energies, experimental X-ray production data at MeV energies are rather scarce. The measurements of σ_p reported in paper IV were undertaken to allow extended comparisons between the theoretical calculations and experimental data at proton energies of several MeV. The results indicate that σ_{ion} values accurate to 10-20 % may be obtained from PWBA and BEA calculations. A "universal" empirical expression is also derived for σ_{ion} by fitting a 5th order polynomial to the experimental data. Cross sections obtained from this equation are estimated to be accurate to 5-10 %, which at the present moment is satisfactory for the elemental trace analysis programme. An analytical expression for the cross sections is very useful both when several experimental arrangements are used as extensive calibration can be avoided and when corrections for the cross section variation with energy loss of the proton has to be done in thick sample analysis.

TESTS OF PIXE

To ensure high quality analytical data numerous tests of the performance of a PIXE system were undertaken. In paper V the linearity of the X-ray intensity vs. the amount of material on the target was investigated experimentally. Other tests included evaluation of the risks of losing material by volatilization of some substances during irradiation in the vacuum chamber. Results from filter samples analysed as part of an inter-laboratory comparison study, quoted in paper V, indicate the quality of the system for homogeneous samples. The ability to obtain good data also on heterogeneous targets was verified in several different experiments. The standard deviation for the set-up was 6 % and for the total analytical procedure 15 %. The accuracy from a series of spotted Mo-solutions evaporated on polystyrene backings is 10 %, but this includes volume uncertainties in the pipette used and possible mechanical losses. The data on the filter samples mentioned indicate about 5 % accuracy. Paper V also contains

discussions of many other aspects of PIXE.

NORTH FLORIDA AEROSOL STUDY

As discussed above, PIXE is favourable when only small samples are available and very low absolute amounts of many elements are to be determined. This is the case in the analysis of impactor collected aerosol size fractions. In paper VI, a model study of the North Florida aerosol is reported as an example of the kind of routine application now made possible using PIXE. The North Florida region was utilized as an environmental setting for the investigation of the generation, transport and removal of natural and pollution aerosols. A five-stage impactor was used to collect samples directly on thin polystyrene backings. Up to 14 elements from S to Br, including Pb, were determined. Means of the size variation trends for different elements were distinctively different suggesting aerosol subpopulations of differing mineralogy and chemical properties. Inter-element ratios and their variation with particle size exhibited considerable constancy over all samples taken, suggesting that localized sources are of less importance than are area sources or long range transport from remote sources. The results of this study demonstrates the value of detailed investigation of a natural environment and its relationships as a background to subsequent research on more complex atmospheric environments that may have been altered by man's activities.

CONCLUSIONS

PIXE is now capable of providing good analytical data and has become a routine method in many laboratories. Like all other analytical methods, certain applications are more attractive than others for the technique and the appropriate analytical method should, of course, be chosen in each case from the premises in the actual situation. Future developments of PIXE are likely to lie mainly in optimization, automation and sample preparation techniques. Using a very well focused beam⁴⁾, impressive spatial resolution is obtainable, opening many interesting fields of PIXE application. Most PIXE work so far has been done on thin samples. Interesting applications are now also being developed on thick samples⁵⁾, extending the applicability

of the method. Future developments of elemental analysis in an accelerator laboratory are also likely to involve other accelerator techniques, those already established or new ones, to increase the information that can be obtained from a given sample.

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X-RAY ANALYSIS: ELEMENTAL TRACE ANALYSIS AT THE 10^{-12} g LEVEL

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Using protons in the MeV region as excitation source and a high resolution Si(Li)-detector, X-ray analysis is capable of detecting many elements at the 10^{-12} g level simultaneously.

The use of X-ray emission analysis for assaying small amounts of trace elements has grown rapidly in recent years. An interesting development has been the introduction of silicon detectors as analyzers giving fast and efficient detection of the X-rays¹). One possibility, which is discussed in the present paper, for increasing the sensitivity of X-ray trace analysis is to use heavy particles for excitation of the X-rays instead of the previously used X-rays or electrons. This has the advantage that the cross section for X-ray production is large and the background contribution from bremsstrahlung is low.

To test this method, a series of experiments has been performed. The material to be analyzed has been deposited on a very thin carbon foil ($40 \mu\text{g}/\text{cm}^2$) and placed in an irradiation chamber connected to the beam pipe of a Van de Graaff-generator. A well-collimated proton beam transverses the sample and the resulting X-rays are recorded by a silicon detector and a 4096 channel analyzer (fig. 1). The energy resolution of the whole system is 0.26 keV, which permits separation and identification of the K_α X-ray peaks from elements with $Z > 15$. The use of thin foils as backing reduces the bremsstrahlung background significantly compared to a thick backing.

As an example of the sensitivity of the method we will describe the analysis of a very dilute solution of a Ti salt (4 ppb of Ti; ppb = part per 10^9). One drop of the solution was evaporated on the carbon foil.

In a 60 min run with a $2.5 \mu\text{A}$ current of 1.5 MeV protons, the spectrum in fig. 2a was obtained. Fig. 2b shows a similar spectrum obtained in 7 min run with a $2 \mu\text{A}$ current on a solution of a Cu salt (80 ppb of Cu).

The amounts of materials detected in these two cases are 4×10^{-11} g Ti and 8×10^{-10} g Cu. It is obvious that the two peaks are very pronounced and that the measured amounts do not represent lower limits of detection. Limits one or two orders of magnitude lower than the values quoted above can probably be realized by accepting smaller peaks and by using longer runs and higher beam currents. As will be discussed below, it is possible to increase the sensitivity even further by optimizing the energy of the proton beam.

An application, which illustrates the usefulness of the method, is investigation of air contaminations. To test the method we placed a carbon foil outdoors for one day and then analyzed it for 60 min with a $2.5 \mu\text{A}$ current. The resulting spectrum is shown in fig. 3. The various peaks correspond to the following deposited amounts of material: 1 ng P, 20 ng S, 100 ng Ca, 1 ng Ti, < 0.02 ng V, 0.06 ng Cr, 0.15 ng Mn, 8.5 ng Fe, < 0.02 ng Cu, 0.4 ng Zn, 0.07 ng Sr, 0.2 ng Zr and 0.3 ng Pb. This example demonstrates both the sensitivity and the possibility of analyzing many elements simultaneously in one single run. Some confusion can arise from interferences between K_α and K_β or L_α and L_β from adjacent elements and between K and L X-rays, but in most cases this is no serious drawback.

In the present experiments one limitation has been the background arising from impurities in the carbon foil. Commercial foils containing small amounts of Cl, Ca, Fe and some other elements have been used. Work is now in progress to prepare ultra-pure foils and there appear to be no difficulties of principle in making foils of reasonable purity.

The experiments performed so far strongly indicate that the present method is promising for elemental trace analysis in the ppb range or lower. It is possible to obtain the amounts of many elements in one single run.

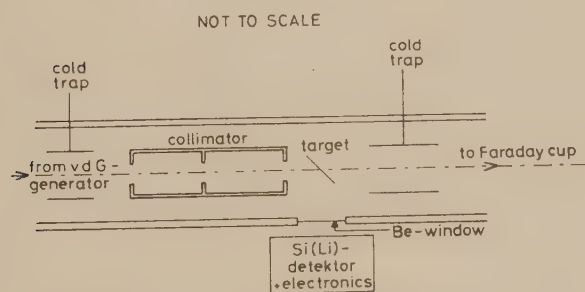


Fig. 1. Experimental arrangement.

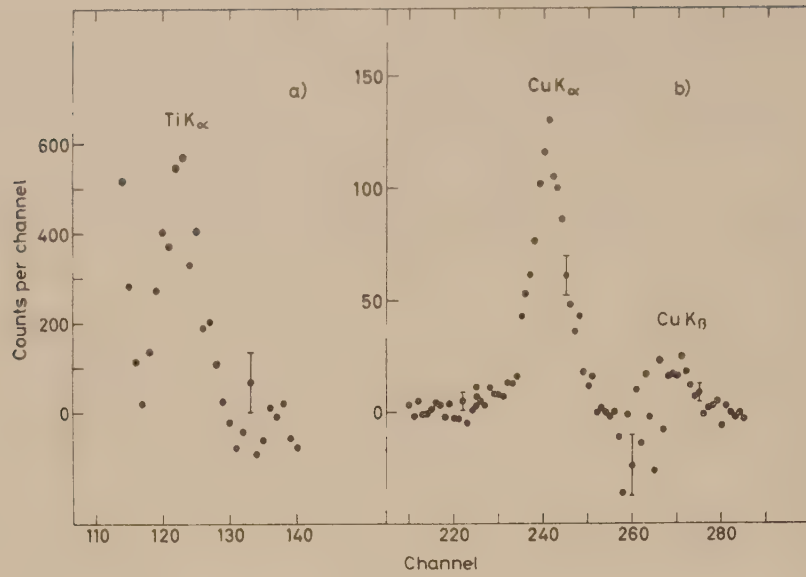


Fig. 2. a) Spectrum of 4×10^{-11} g Ti obtained in a 60 min run. The points to the left are from a Ca-impurity. b) Spectrum of 8×10^{-10} g Cu obtained in a 7 min run. In both spectra background has been subtracted. The indicated errors are statistical.

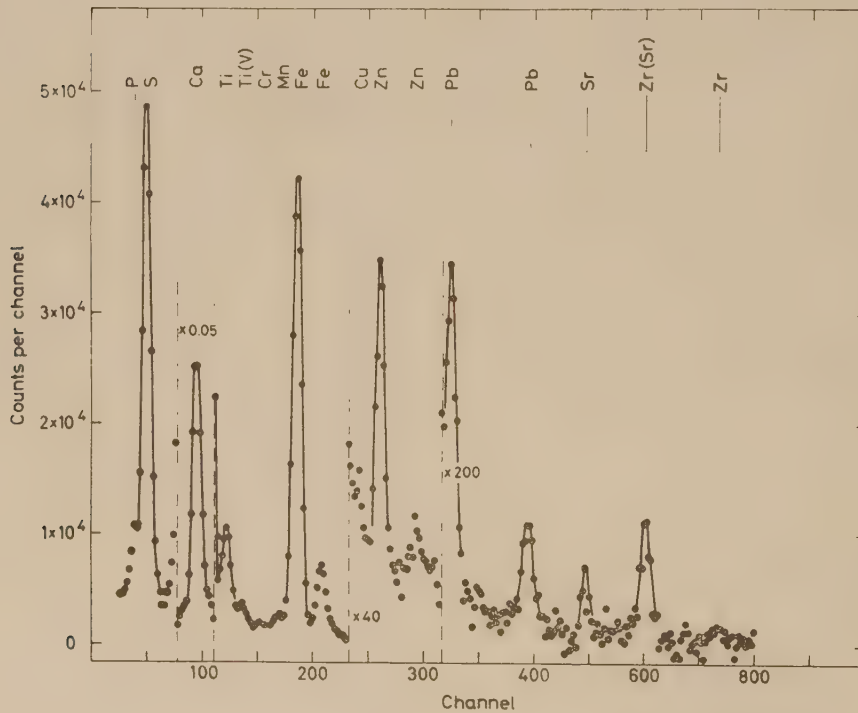


Fig. 3. Spectrum from a carbon foil placed outdoors for one day. The peaks correspond to the K_α and K_β lines of the elements deposited. For Pb, the peaks arise from L-radiation.

ELEMENTAL TRACE ANALYSIS AT THE 10^{-12} g LEVEL

If the elements are present in comparable quantities, the method covers the whole periodic system from around P and upwards. Of course, not only water solutions but also thin samples of all kinds can be analyzed, as well as thick samples. In the latter case however, the background contribution from bremsstrahlung will be large. In many situations, the analyzing conditions can be improved by using suitable absorbers between target and detector, thus increasing the relative yield of the interesting peaks. As an example of an application of this type we have determined trace amounts (1 ppm) of silver in a pure copper foil.

In the present, exploratory investigation the experimental conditions have not been optimized for maximum sensitivity. The greatest gain can be obtained by increasing the energy of the proton beam. The cross section for K X-ray production has a maximum, which for example comes at ≈ 10 MeV for $Z \approx 30^2$). Compared to the present experiment, in which the proton energy was 1.5 MeV, the cross section increases with a factor of 20.

The theoretical lower limit of detection can be calculated in the following way. The total number of counts N in a peak corresponding to A atoms of an element in a sample is

$$N = An\sigma\omega(\Omega/4\pi)\varepsilon,$$

where n is the total number of protons per cm^2 , σ the cross section for ionization of the shell in question, ω the fluorescence yield for the particular X-ray peak used in the measurement, Ω the solid angle subtended by the detector and ε the efficiency of the detector.

To obtain the lower limit, we set $N = 100$. Since the background is low (about 150 counts per keV in 30 min at 20 keV with a $5 \mu\text{A}$ current) this value corresponds in general to a well-defined peak. If the spectrum contains a very strong peak, this, of course, gives an increased background for neighbouring elements. Furthermore, we use for n a value corresponding to a 30 min run with a current of $5 \mu\text{A}$. σ is taken from ref. 3 and ω from refs. 4 and 5. The distance between target and detector is assumed to be 5 cm and $\varepsilon = 0.95$. For a proton energy of 1.5 MeV and measurements on the K lines the following lower limits are obtained: 0.3×10^{-12} g Ca, 10^{-12} g Cu and 20×10^{-12} g Ba. For heavier elements the best results are obtained by

measuring on the L lines and here, as an example, the lower limit is 10^{-11} g for Pb. The calculated values are in accord with the experimental results. If, instead, the proton energy corresponding to the peak of the theoretical cross section curve is used, the following limits are obtained: 7×10^{-14} g Ca, 5×10^{-14} g Cu and 2×10^{-14} g Ba.

A further possibility of increasing the sensitivity is to use multiply-charged ions. The cross section for X-ray production is proportional to the square of the charge. Since heavy ions up to argon are accelerated in many laboratories, there appears to be a real possibility to get a further increase in sensitivity and to obtain a limit of detection well below 10^{-15} g. However, before such a sensitivity can be of practical use many problems have to be solved, especially the background problem. In most cases, the thin sample to be analyzed has to be supported in some way. The purity of the commercially available high-purity materials is too low for this purpose and therefore considerable work has to be done on the purification of the supporting foils as well as on materials and chemicals used in preparing the samples. Another source of impurities is the residual gas in the accelerator and irradiation chamber. Even if the vacuum is good, according to normal accelerator standards, there are enough impurities to give strong background peaks. Cold traps and other precautions are therefore necessary to reduce this type of background. Problems may also arise with certain targets when they are placed in vacuum and irradiated.

Despite these difficulties the limit of detection obtained so far is of the order 10^{-11} g. With minor improvements to our present apparatus the 10^{-12} g level can definitely be reached. The above theoretical extrapolation shows that the 10^{-15} g level might be attainable.

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A BEAM MAPPING METHOD

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The article describes a method to examine the particle distribution in a beam by moving a small probe in it and measuring the characteristic X-rays derived from the probe.

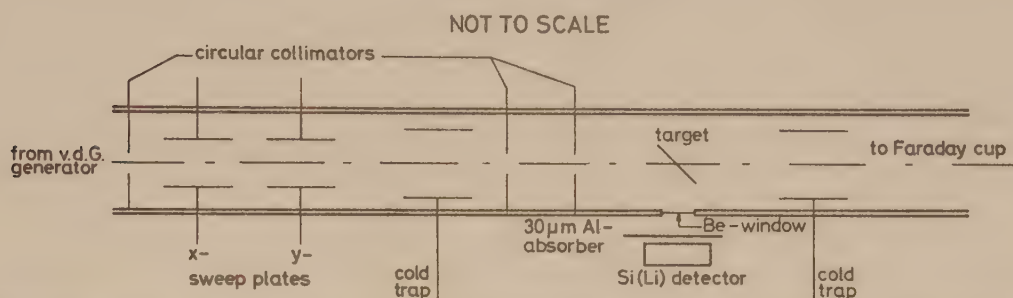


Fig. 1. Experimental set-up. The proton beam is swept electrostatically by triangular waves applied to parallel plates in the beam tube. The maximum amplitudes are sufficiently large to sweep the focused beam out of the collimator hole. The frequencies are 33 Hz in the x - and 262 Hz in the perpendicular y -direction. The Al-absorber allows the detector to be moved near the target, since it reduces the amount of low energy X-rays to the detector. The target transportation arrangement is not shown.

In various experiments with particle accelerators, knowledge of the distribution of particles in a plane perpendicular to the beam is needed. Especially, the use of particle-excited characteristic X-rays in trace analysis, has made this necessary¹).

It is possible to examine the particle distribution in a beam, by moving a probe in it measuring the prompt radiation from the probe as a function of its position in the beam. To get a good resolution the probe has to be small compared to the beam dimensions. This makes it necessary to utilize a reaction with a high cross section to get reasonable counting times. Particle-excited characteristic X-rays are suitable for this purpose. By putting the cross section as a function of the particle energy and Z of the target material a smooth surface is obtained, which offers a possibility to examine the distribution for any particle energy. For MeV protons the K X-ray production cross sections are large, e.g. 924 b for 1.7 MeV protons on Al²) and 294 b for 5 MeV protons on Ni³). The easiness in interpreting these measurements makes this method

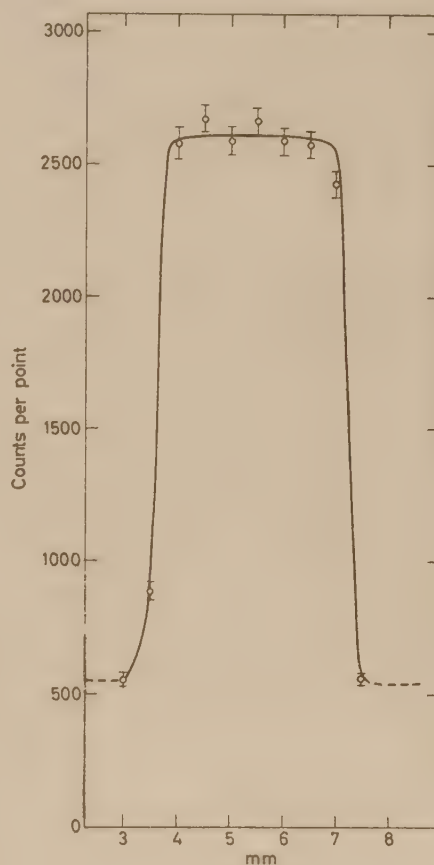


Fig. 2. A typical profile through the proton beam. The used proton beam collimator was 4 mm in diameter. The indicated errors are statistical. The points are normalized to the same solid angle.

superior to the common method of measuring the current from a movable string in the beam.

To measure the distribution in the proton beam used in our experiment a thin piece of silver (area ≈ 0.05 mm²) was put as probe on a carbon backing (40 $\mu\text{g}/\text{cm}^2$), and this target was mounted in a chamber where it could be moved in two perpendicular directions with micrometer screws. Silver was chosen because the energy of its K-radiation is in an interval where background from impurities in our carbon foil is low.

2 MeV protons were used and the number of silver K $_{\alpha}$ X-rays was measured with a Si(Li)-detector. A single channel analyser window was placed over the K $_{\alpha}$ -peak and the number of counts in a run was recorded with a scaler. This number was normalized

to the proton charge 120 μC , which was obtained in about 3 min.

Fig. 1 shows the experimental set-up and fig. 2 a typical profile of the beam measured by this method.

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PROTON-INDUCED X-RAY EMISSION SPECTROSCOPY IN ELEMENTAL TRACE ANALYSIS

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ABSTRACT

Using protons in the MeV range as excitation source and a high resolution Si(Li) detector, X-ray emission spectroscopy is shown to be capable of analysing many elements with $Z > 15$ simultaneously at the 10^{-12} g level. This work discusses a theoretical lower limit of detection at moderate proton energies and gives examples of possible applications: analysis of the elemental composition of air-borne particles as a function of particle size, oil slick identification, and analysis of water and blood serum.

INTRODUCTION

X-ray emission analysis has long been applied to trace element analysis. Photons and electrons have hitherto mostly been used as excitation sources and the characteristic X-rays have been analyzed by crystals or low resolution proportional and scintillation counters.

The introduction of high resolution semiconductor detectors has, however, opened the way for fast and efficient detection of the X-rays. This has made multi-elemental analysis much more attractive since the time required is greatly reduced. In recent years, heavier particles have also been used for excitation of characteristic X-rays from a sample.

Important factors determining lower limits of detection are X-ray production cross sections, the available flux of exciting particles or photons and background conditions.

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The cross sections for photon excitation are rather large. When photons are used, the limitations come from the difficulty of producing strong radioactive sources and from the background of scattered photons.

Electrons are used in micro-analysis in connection with electron-microscopes and extremely small amounts ($\sim 10^{-14}$ g) have been reported as the lower limit of detection. Very small samples are then analyzed, however, so the concentrations detectable tend to remain in the 0.01 % region. A serious drawback with electrons is the background arising from bremsstrahlung.

In a report to this conference last year, Needham and Sartwell (1) discussed proton excitation in the energy region of 100 keV. In a recent report we have discussed the use of MeV protons in trace analysis (2). Watson et al have investigated the analytical capabilities of high energy alpha particles as exciting particles (3). Heavy particles produce considerably less intense bremsstrahlung than electrons thereby reducing the background. The ionization cross sections are also higher, thus making these sources of excitation attractive. Contrary to photons, intense beams of charged particles can easily be produced.

The cross sections for X-ray production by heavy ion irradiation are two to three orders of magnitude larger than the cross sections for protons in the same energy range (4). Extremely small quantities should in principle be detectable using heavy ions although the amount of material that can be analyzed is limited by the small penetration depth.

In the present paper we give a further discussion of proton excitation and give a few examples of possible applications.

THEORETICAL

A theoretical lower limit of detection can be calculated in the following way. The total number of counts in a peak corresponding to A atoms of an element in a thin sample is

$$N = A n \sigma \omega k(\Omega/4\pi)\epsilon \quad (1)$$

where n is the total number of protons per cm^2 , σ the cross section for ionization of the shell in question, ω the fluorescence yield, k the relative transition probability for the particular X-ray peak used in the measurement, Ω the solid angle subtended by the detector and ϵ the efficiency of the detector.

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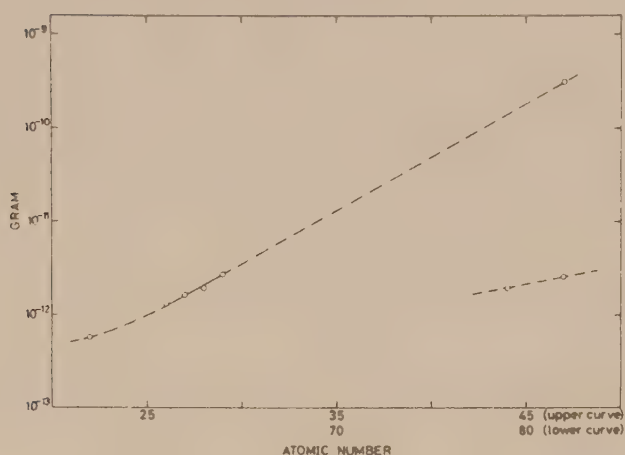


Figure 1. Lower limit of detection for different elements.

In figure 1 we present lower limits of detection for a part of the periodic table. The calculations are made for protons of 2.5 MeV, the energy given by our accelerator. For the beam current and analyzing time, we have chosen values of 1 μ A and 30 minutes giving a total charge of 1.8 mC through the 4 mm diameter collimator. The detector is also assumed to be placed 50 mm from the target.

The number of counts, N , needed to give a well defined peak is assumed to be 100. This is a conservative figure at X-ray energies above 10 keV but at lower energies the background contains several peaks from contamination in the sample backing which in some cases will present problems.

The calculations are made for the most intense peak from each element using relative X-ray transition probabilities from Hansen et al (5). The X-ray production cross sections used are taken from recent measurements in this laboratory (6). They are in agreement with measurements by Bissinger et al (7).

For heavy elements, the L X-rays are used since the L X-ray production cross sections are much larger than the corresponding K X-ray cross sections and the L X-ray energy is more suitable for analyzing with Si(Li) detectors.

As demonstrated by Bissinger et al the ionization cross sections increase with the proton energy and have a maximum which for medium-heavy elements e.g. nickel occurs at ~ 15 MeV, where the cross section is 1500 barns compared to our value of 200 barns at 2.5 MeV. Thus, by increasing the proton energy it is possible to reduce the lower limits of detection further.

EXPERIMENTAL

For quantitative analysis it is necessary to know the distribution of target atoms over the irradiated surface and the distribution of particles in the beam. If one of these quantities has a rectangular distribution the calculations are simplified. From formula (1) we have

$$N = \text{const} \int n(s) A(s) dS \quad (2)$$

where $n(s)$ and $A(s)$ are functions describing the distribution of protons and target atoms over the irradiated area, S . As we usually do not know the distribution of the target atoms, we have chosen to arrange so that the protons have a rectangular distribution. This is made by sweeping the well-collimated beam in two perpendicular directions using deflecting voltages in the form of symmetrical triangles with frequencies of 116 Hz in one direction and 1250 Hz in the other. This arrangement gives the desired proton distribution (8). Equation (2) then simplifies to

$$N = \text{const} n \int A(s) dS = \text{const} n A_{\text{tot}} \quad (3)$$

which simply requires that all the atoms to be analyzed are in the irradiated area. This condition is fulfilled in the measurements.

The set of collimators just before the target includes a quartz glass with a hole slightly larger than the collimators. By turning a protecting tantalum collimator away, the intensity distribution in the beam can be observed and the sweeping voltage adjusted to a proper value. In selecting this, it is important to bear in mind that the momentary counting rate in detector and electronics is determined by the momentary beam current.

The charge passing through the last collimator is collected in an isolated cup (see figure 2) earthed through a commercial current digitizer. Thus the current passing through the target can be measured accurately. The current digitizer has been checked to be better than 1 %. Behind the last collimator a ring of pure aluminum is placed. We keep this plate at a potential of -150 V to suppress secondary electrons from the target, which would otherwise interfere with the current measurement. This interference is in the order of 10 %.

The samples to be analyzed are placed on thin self-supporting carbon foils ($20 \mu\text{g}/\text{cm}^2$), which cover a hole in a pure aluminum frame. Six frames are placed on a ladder, which is inserted in the irradiation chamber through a vacuum lock.

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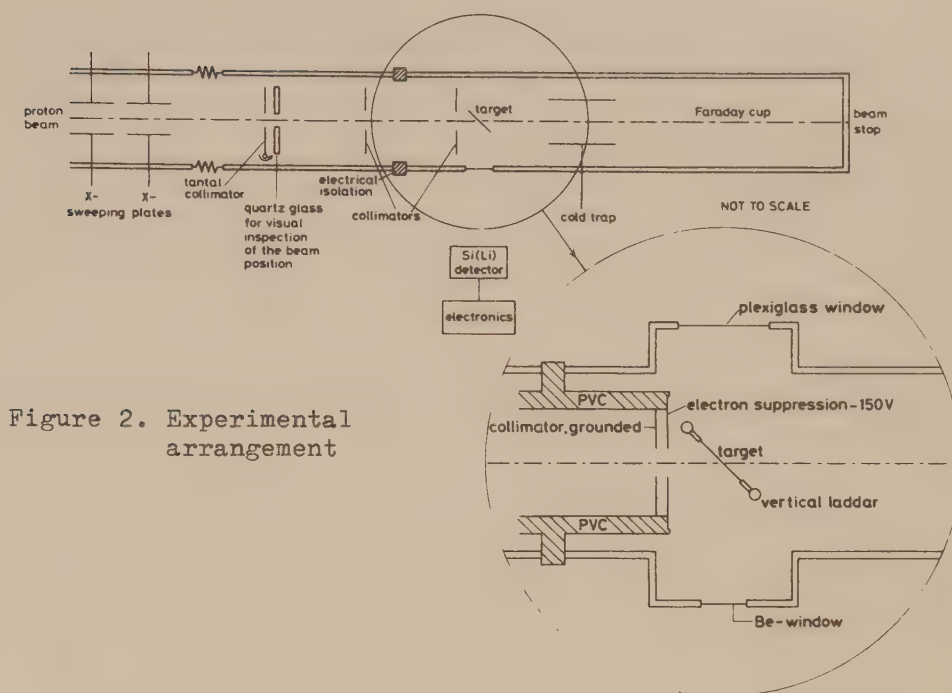


Figure 2. Experimental arrangement

The samples are thin to protons and X-rays. This is implicitly assumed in formula (1), where we should otherwise have to integrate over the proton.

The detector is a Si(Li) detector with a cooled FET-transistor in the first preamplifier stage. The pulses are amplified in conventional amplifiers and analyzed with a multi-channel analyzer. The detector area is 26 mm^2 . The system resolution is 0.26 keV FWHM . The spectra are punched on paper tapes for further processing in a computer. The analyzing program is a version of SAMPO (9). Some confusion in analyzing the spectra may arise from interferences between K_{α} and K_{β} of adjacent elements or between K and L radiation from different elements. For example $L_{\alpha 1}$ of lead and $K_{\alpha 1}$ of arsenic are separated by only 8 eV . When such ambiguity arises, it is necessary to make use of the relative X-ray transition probabilities to assist in unravelling the spectrum.

Background

A low background is necessary if small quantities are to be measured. The background from our carbon foils is $300 \text{ counts per keV and mC}$ at energies over 10 keV with a target-detector

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distance of 5 cm. At lower energies impurities in the carbon foils increase the background. Elements such as calcium, iron, copper and zinc are present in rather large quantities. The foils may contain as much as 100 ng calcium, while the others are present in the 100 pg range within the irradiated area. Other light elements may also be present. The large amount of calcium gives rise to a high counting rate forcing us to use lower beam currents or to insert an absorber such as aluminum. The preparation of pure backing foils is at present a major factor limiting the usefulness of the method. Work is now going on to improve the carbon foils.

Other backing materials such as hostaphan or thin aluminum foils have also been tried. The background from hostaphan ($350 \mu\text{g}/\text{cm}^2$) and aluminum foils ($1 \mu\text{m}$ thick) were found to be four times the background from carbon foils.

To get some experimental information about the lower limit of detection we placed small amounts of chromium on a carbon foil. The foil was first analyzed and found to contain a small amount of chromium. The background in this energy region is unfavourable, with a chromium peak situated on the side of a huge calcium peak. This latter peak was reduced by the use of aluminum absorbers but was nevertheless about 1000 times as high as the chromium peak. Various amounts of chromium were then placed on a carbon foil using a diluted water solution of $\text{Cr}(\text{NO}_3)_3$, molybdenum being added to the solution as a carrier. Figure 3 shows the peak imposed on the side of the calcium peak in a run after the addition of 10 pg chromium. The peak was obtained in a two hours run with a total charge of 3.5 mC passing through the target. The collimator diameter was 5.5 mm and the target-detector distance 50 mm with a $30 \mu\text{m}$ aluminum-absorber inserted. The peak in figure 3 corresponds to about 30 pg chromium. Hence most of it is background.

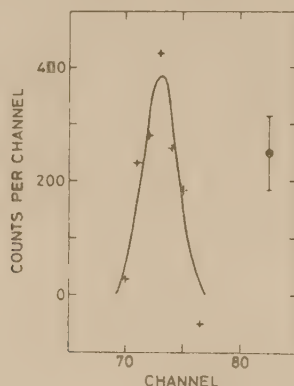


Figure 3. A chromium-peak after background subtraction. The peak corresponds to 30 pg of chromium.

Table 1

The mass of some elements in air-borne particles of different sizes from one cubicmeter of air. The sample is collected a rainy day in June 1971 in the outskirts of Lund.

Aerodynamic particle size interval (μm) (theoretical)	Mass per particle size interval $\times 10^{-10}\text{g}$ per cubicmeter air			
	Pb	Br	Mn	Zn
1 - 2	25	6	0.3	7
2 - 5	3	2	0.1	5
5 - 9	2	0.5	1.5	13
> 9	-	-	0.6	1

particles and integrates over all sizes of sedimenting particles. Filters of various kinds are generally used in the study of air-borne particles. These sampling methods give the total mass but do not give information about the size distribution. The aerodynamic size distribution, for example, determines the amount of particles that is deposited in different parts of the air-passages (10). A method to collect particles differentiated in size classes is to use cascade impactors (11,12). Generally only the weight distribution has been studied, but recently chemical analysis has been reported (13).

For a preliminary experiment we constructed a cascade impactor. The air is drawn through successive holes of decreasing diameter and a glass slide covered by a carbon foil is placed perpendicular to the air jet. The cut-off diameters have not been measured but calculated (11). After collecting particles the carbon foils are transferred to the aluminum frames and irradiated. Figure 4 shows a typical spectrum obtained in this type of analysis. The spectrum was obtained in 45 min and 1 mC of 2.5 MeV protons passed the target. The target-detector distance was 50 mm and a 30 μm aluminum absorber was inserted. The spectrum corresponds to an aerodynamic particle diameter of 5-9 μm . The peaks not mentioned in table 1 belong to the background. Table 1 gives an example of the kind of information obtained by this type of air-borne particle studies. In the table a difference is indicated in the composition of particles of different sizes.

Identification of Oil Samples

In an extensive study Bryan et al (14) have shown the possibility of identifying oil slicks by using their elemental content as "finger prints". These workers used neutron activation analysis to investigate the elemental content of 40 oil

Table 2

The concentrations of some elements in a sample of crude oil and theoretical lower limits of detection.

Element	ppm found in a sample of crude oil	Theoretical lower limit of detection (ppm)
Ti	1	0.0006
V	2	0.0007
Fe	3	0.001
Ni	0.2	0.002
Cu	3	0.002
As	0.2	0.008
Mn	traces	0.0008
Br	< 0.003	0.01
I	< 0.5	2 (K X-rays)
Ga	< 0.001	0.005
Ba	-	3 (K X-rays)

samples. 22 elements were found in various samples. Three general categories of usefulness were specified: Group I: vanadium, manganese, bromine, nickel, sulfur, aluminum, iodine, gallium, barium and arsenic were considered to be "fundamentally useful by virtue of their frequency of encounter and their concentration range". Group II: zinc, indium, tin, cobalt, molybdenum, lanthanum, strontium and gold were considered to have "supplementary usefulness by virtue of their rare occurrence" and group III: sodium, chlorine, antimony and samarium were dubious for various reasons. All elements in group I and II except aluminum can be analyzed by our method. To determine the oil quantity analyzed we added an internal standard, strontium-cyclo-hexanbutyrate in a strontium concentration of 10 ppm. The amount of oil analyzed was determined to be about 1 mg. In preparing an oil sample one drop of the oil with the internal standard added is placed on the carbon foil, which has already been mounted on the aluminum frame. The sample is then slowly warmed up to about 180° C. When the lighter fractions evaporate, the oil thickens enough to be put into the beam. When the beam hits the sample, the oil is smoothed out on the foil. In table 2 is shown the recorded concentrations in a sample of crude oil. The vanadium content of this sample was analyzed by the company supplying the oil and found to be 1.3 ppm. The values were obtained in a run with 2.5 MeV protons for 60 minutes giving a total charge of 6 mC. The target-detector distance was 47 mm and a 30 μ m aluminum absorber was inserted between target and detector.

In the table are also shown lower limits of detection for the group I elements. The limits are calculated from the

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assumptions made earlier in this paper assuming an analyzed amount of 1 mg of oil. These limits indicate that about the same information that is obtainable with neutron activation analysis can also be gathered in a single run with our method.

Water Analysis

Water samples are easily prepared. A drop of water is placed on a carbon foil and after evaporation of the water the sample is ready to be irradiated. In order to develop a method for geological prospecting we have made some work on ground water samples. These samples were first pre-concentrated seven times by evaporation. A drop was then analyzed. In figure 5 we show a typical spectrum obtained in a run with 2.5 MeV protons in 130 min. A charge of 8 mC passed the target. The

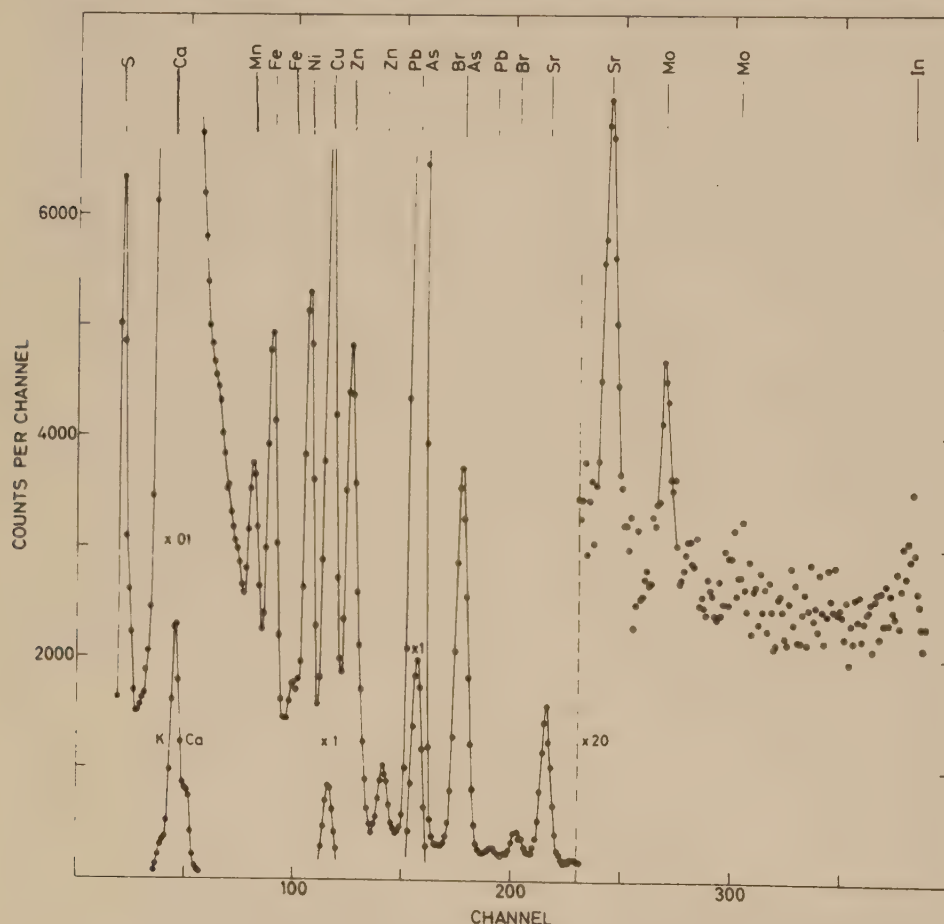


Figure 5. A pulseheight spectrum from analysis of a water sample. The background has not been subtracted.

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Table 3
The concentrations of some elements in a water sample.

Element	Measured "concentration" not corrected for back- ground	Concentration present in the sample (after subtrac- tion of background) from the carbon foil
Ca	3 ppm	1 ppm
Ti	17 ppb	-
Mn	4 "	4 ppb
Fe	9 "	-
Ni	14 "	14 "
Cu	31 "	-
Zn	20 "	-
As	190 "	190 "
Br	21 "	21 "
Sr	47 "	47 "
Mo	11 "	10 "

target-detector distance was 50 mm and a 30 μ m aluminum-absorber was used. Table 3 presents the total concentrations as well as the concentrations after subtraction of the background.

Analysis of Blood Serum

Determination of elements in blood serum is another problem we are investigating (15).

In a recent report Niedermeier et al (16) describe an emission spectrometric method of analyzing blood serum and other biological fluids. After wet ashing the sample was excited in a 10 a dc arc. For example a threshold value for iron as low as 1.6 μ g/100 ml was reported.

Evaporation of blood serum on a carbon foil as in preparation of water samples does not work since the contraction of the serum tears the foil. Hostaphan foils (350 μ g/cm²), are, however, strong enough to withstand these forces and can be used. Another problem arises when irradiating the samples. There is a tendency that the sample will become detached from the backing. Therefore we had to cover the serum sample, after evaporation of the water, with another hostaphan foil. This arrangement worked quite well. An advantage of this preparation is that no chemistry has to be made on the sample. In figure 6 we show spectra with and without serum for iron. The spectra were obtained in 60 minutes runs with a beam current as low as 50 nA, due to the risk of destroying the hostaphan foils. The amount of serum was 15 mg. The iron content in the serum sample was

calculated to be $53 \mu\text{g}/100 \text{ ml}$ compared with the figure of $61 \mu\text{g}/100 \text{ ml}$ obtained with standard atomic absorption methods.

From the spectra in figure 6 a lower limit of detection about $1 \mu\text{g}/100 \text{ ml}$ of serum can be estimated, assuming as the criterion of detection that the iron-peak is to be increased to four times the standard deviation by addition of the serum. It should be possible to reduce the background further and thus decrease the lower limit of detection.

In our spectra we have also observed elements such as copper, bromine and zinc. As the sensitivity of existing methods generally is sufficient for routine analysis, the advantage in using the present method is that most elements will be determined simultaneously and that elements occurring in very low concentrations can also be detected.

DISCUSSION

The use of proton-excited characteristic X-rays in trace analysis has shown to be applicable down to 10^{-11} g when 2.5 MeV protons are used. A limiting factor is the purity of the backing material which, at the present moment, prevents us, especially for medium-heavy elements, making full use of the high sensitivity of the method. As shown in the above theoretical considerations a lower limit of detection at the 10^{-12} g level is readily achieved when backing material without larger impurities is available. The ionization cross sections can be increased by a factor of at least 5 by choosing

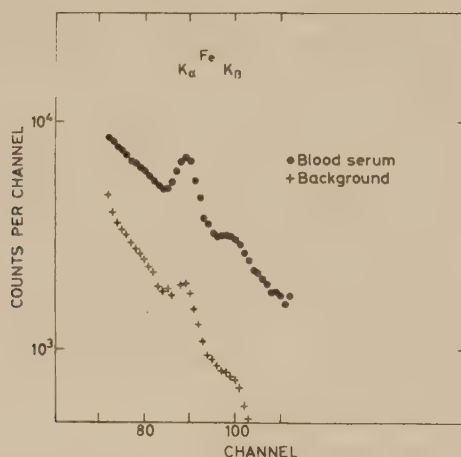


Figure 6. A pulseheight spectrum from analysis of iron in blood serum.

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higher proton energy. This, and the possibility of using higher beam currents in some applications, as well as increasing the analyzing times may reduce the lower limit of detection further. The very high ionization cross sections obtainable with heavy ions might also permit a further reduction in the lower limit of detection.

Methods for trace analysis generally use known samples to establish a calibration curve. The parameters determining the response from the proton beam are all known or possible to determine for a run. Thus it is possible to determine the present amounts from a simple calculation. Especially when multi-element analyses are made, this simplifies the procedure.

Compared with most methods of trace analysis, one great advantage of our technique is its capability to determine most of the elements present in a single run. This is already demonstrated in the spectra shown above, where, in spite of a rather poor resolution compared with that of the most recent detectors, many elements have been determined simultaneously. Since the interest in determining all the elements present in a single run is great, this reduces considerably the time needed for analysis. The improved resolution of the detectors also gives narrower peaks, thereby increasing the signal-to-background ratio.

A further advantage of this method compared with many other methods of trace analysis is the rather small variation in sensitivity between different elements.

Together with the lower limit of detection expressed in weight terms, the same quantity expressed in concentration terms is of interest. For example, the very low amounts of an element detectable with the electron microprobe must be present in very small samples, thus the concentration of the elements must be rather high to be detected.

The stopping power of material is in the order of 100 keV/mg/cm^2 for 2.5 MeV protons, which allows us to use rather thick samples without destroying the thin target assumption. This makes it possible not only to detect small amounts but also small concentrations.

ACKNOWLEDGEMENTS

Mr K. Håkansson and Mr C. Nilsson provided the proton beam and Mr K. Sjöberg built our apparatus. Their skilful assistance is greatly acknowledged. The work has been sponsored by the Swedish Board for Technical Development.

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X-Ray Production by 1.5–11 MeV Protons

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Abstract. *K*-shell ionization and *L* x-ray production cross-sections by proton impact have been determined from measurements of *K* x-ray yields from thin targets of Ti, Fe, Co, Cu, Ni and Ag and of *L* x-ray yields from Au and Pb. The proton energies varied from 1.5 to 11 MeV. A Si(Li) semiconductor detector recorded the x-rays. The total error in the measured cross-sections is mostly less than 5%. K_{β}/K_{α} ratios and $L_{\text{I},\beta,\gamma}/L_{\alpha}$ ratios have been determined. Ionization cross-sections have been compared with predictions of the plane-wave Born approximation (PWBA) and the binary-encounter approximation (BEA). Both theories describe the ionization quite well: PWBA is, however, better for higher proton energies whereas BEA is superior for lower energies. An empirical formula for ionization cross-sections is derived.

Introduction

Since their original discovery by Chadwick in 1912, heavy charged-particle induced characteristic x-rays have attracted continued interest and, in 1958, Merzbacher and Lewis [1] published an extensive review article.

Ionization cross-sections by heavy charged-particle impact have generally been compared with predictions of the plane-wave Born approximation (PWBA). This model describes the qualitative behaviour of the cross-sections as a function of the impinging particle energy quite well, but does not give a good quantitative description of the cross-section at low proton energies. At MeV energies, the model seems to be better, although available experimental results are scarce. Low-energy cross-sections appear to be better described by the semiclassical approach by Bang and Hansteen [2], who take the deflection of the proton in the Coulomb field of the nucleus into account. The binary-encounter model developed by Garcia [3] seems to provide ionization cross-sections in good agreement with experimental data at both high and low energies.

Most published experimental work has been done with low-energy protons. Modern work with proton energies above a few MeV are reported by Bissinger *et al.* [4, 5] using 2–28 MeV protons impinging on Ca, Ti, Ni and Ag and by Jarvis *et al.* [6] using 160 MeV protons impinging on 15 elements between $Z=26$ and 92. In addition, Watson *et al.* [7] have measured *K* or *L* x-ray cross-sections for 13 elements using 30–80 MeV α -particles. Very recently, Barse *et al.* [8] measured K_{α} and L_{α} x-ray production cross-sections using 1 to 3.7 MeV protons for 11 and 10 elements respectively and Winters *et al.* [9] studied inner shell ionization of Ar, Kr and Xe by 1.5 to 5.0 MeV protons. In these works errors of 10–20% are reported.

Measurements of ionization cross-sections in the 1950-ies were generally made using thick targets and scintillation detectors. The high resolution Si(Li) detectors now available provide superior conditions for this type of work. Ref. [1] contains references to the older literature, while references to later work can be found in Ref. [10].

Incentives to the present work were to extend the possibilities of comparing calculations of x-ray ionization cross-sections with precise measurements at MeV energies and to provide the sensitive method of elemental trace-analysis offered by using MeV protons

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to excite characteristic x-rays from a sample [11, 12], with accurate x-ray production cross-sections.

Measurements with a total error of typically 5% or less of *K* x-ray production cross-sections have thus been performed for protons of energies between 1.5 and 11 MeV impinging on Ti, Fe, Co, Ni, Cu and Ag and of *L* x-ray production cross-sections in Au and Pb using protons of the same energies.

Experiment

A. Apparatus

Proton beams were obtained from the 3 MeV Van de Graaff accelerator at the University of Lund and, for energies higher than 3 MeV, from the 12 MeV Tandem Van de Graaff accelerator at the University of Uppsala. To compare the different accelerator set-ups with each other, some of the targets were used at 3 MeV at both accelerators. The differences between these measurements are consistent with the experimental error.

The design of the target chamber and collimator arrangements used at both accelerators is outlined in Fig. 1. The beam passes a pair of sweeping plates in the Lund experiments to get a uniform proton distribution on the target [13], and then a cold trap and a set of collimators before penetrating the target foil.

One of the collimators is made of quartz glass to allow us to observe the size of the swept beam. The last collimator, an aluminum plate with a 4 mm diameter hole, was situated about 3 cm from the target foil. Before the target and just behind the last collimator an aluminum disc at a potential of -350 V and with a hole slightly larger than that of the collimator was

placed to suppress secondary electrons from the target. The Faraday cup collected all the charge passing through the last collimator. The set-up is similar to the one used for the trace-element analysis program in this laboratory.

A current digitizer integrated the beam current. Its accuracy and precision were tested to be better than 1% using a stable bias coupled over a precision resistor (0.1%) as a current source. The current was measured using a high-impedance digital voltage instrument coupled over the precision resistor.

The distance between the target and the detector was varied in the range 0.7 to 2 m to achieve a suitably-low counting-rate.

The x-rays were taken through an evacuated pipe which was 42 mm wide and had a 18 mm collimator inserted halfway to the detector to prevent any coherently scattered photons from reaching the detector. Only a thin Be-window and a few mm of air separated the accelerator vacuum from the detector. The background was kept low using lead to shield the detector at higher proton energies.

B. Detector and Electronics

An Ortec Si(Li) detector with 0.27 keV resolution (FWHM) at 6.4 keV recorded the spectra. The efficiency of the detector was measured with carrierfree radioactive sources supported by thin plastic backings purchased from AB Atomenergi, Studsvik, Sweden. Calculations showed negligible x-ray absorption in the sources. The activities of the sources were determined by the manufacturer by comparison with absolute-calibrated standard sources from the Radio-

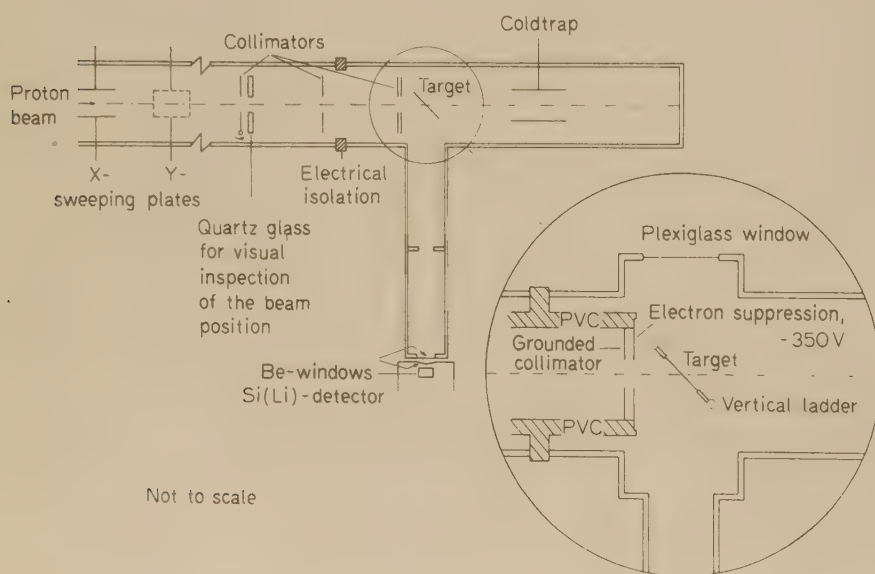


Fig. 1. Experimental arrangement

X-Ray Production by 1.5–11 MeV Protons

Table 1. Detector efficiency calibration with radioactive isotopes. P_K is the fraction of electrons captured from the K shell in the decay. ω_K is the fluorescence yield

Source	$E(K_\alpha)$ (keV)	$P_K \omega_K^a$	EC^a	Activity (10^4 s^{-1})	Transmission		ϵ
					air	hostaphan	
^{54}Mn	5.41	0.2510	1	3.404	0.957	0.984	0.783 ± 0.012
^{57}Co	6.40	0.547 ^b	1	4.048	0.974	0.991	0.872 ± 0.021
^{65}Zn	8.05	0.3885	0.9855	3.698	0.987	0.995	0.982 ± 0.014
^{85}Sr	13.39	0.5959	1	35.34	0.998	1.000	0.978 ± 0.024
^{88}Y	14.16	0.634	0.9979	38.30	0.999	1.000	0.975 ± 0.015
^{57}Co	14.40	0.094 ^b	1	4.048	0.999	1.000	0.944 ± 0.023
^{125}I	27.4	^c	—	2.12	1.000	1.000	0.74 ± 0.06

^a Ref. [14].

^b K x-rays per decay.

^c $\omega_K \left(P_K + \frac{\alpha_K}{1 + \alpha_T} \right) k = 1.130$, where $\omega_K \left(P_K + \frac{\alpha_K}{1 + \alpha_T} \right)$ is calculated from values given in Ref. [15] and $k = I(K_\alpha)/(I(K_\alpha) + I(K_\beta)) = 0.813$ is calculated from the $I(K_\beta)/I(K_\alpha)$ -value measured by Hansen *et al.* [16].

chemical Centre at Amersham, England. Table 1 contains the data used for the efficiency calculation. The efficiency measurements were made at very low counting rates (<10 pulses per sec) using a source holder that allowed us to maintain a vacuum over most of the distance (102.75 ± 0.30 mm) between the source and the detector. The only absorbers were 11.6 mm air and a 6 μm thick Hostaphan foil (see Table 1). The Be-window from the target chamber was used and the detector efficiency thus includes all absorbers present in the cross-section measurements.

The result of the efficiency measurements is shown in Table 1 and in Fig. 2. The effective detector area at 6.4 keV was calculated to be $25.99 \pm 0.07 \text{ mm}^2$ from measurements with and without a collimator of well-known size. This area might be energy-dependent due to absorption in an annular dead layer [17, 18], however, when calculating the x-ray production cross-sections, the area cancels out. Also shown in Fig. 2 is a calculated efficiency curve supposing a sensitive depth of 3 mm and absorption layers of 0.25 mm Be, 40 $\mu\text{g}/\text{cm}^2$ Au and 1 μm Si.

The Si x-ray escape probability is taken from Freund *et al.* [18]. Other reasonable combinations of the thicknesses of the absorbing layers also fit the experimental points giving high uncertainty at low energies. At 4.51 keV, which is the lowest energy used in this experiment, the uncertainty is estimated to be 5%, in the range 6–9 keV 3%, in the range 9–17 keV 2% and for Ag K x-rays 2.5%.

Fig. 3 shows the detector set-up and the electronics used. The main amplifier was operated with 3 μs time-constants.

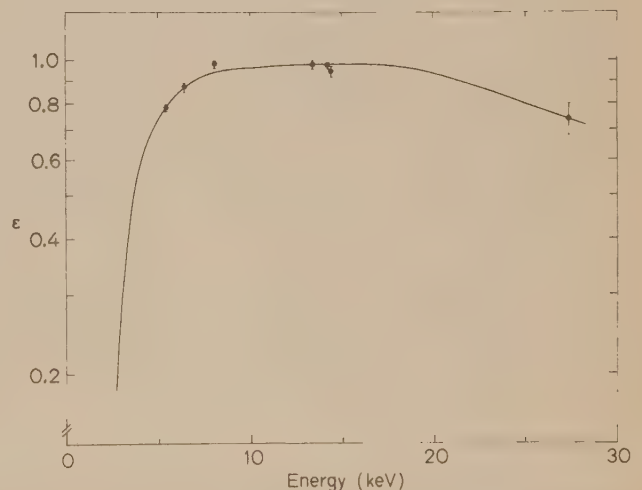


Fig. 2. The efficiency of the Si(Li) detector. The curve is calculated assuming a sensitive depth of 3.0 mm and absorption in 0.25 mm Be, 40 $\mu\text{g}/\text{cm}^2$ Au and 1 μm Si

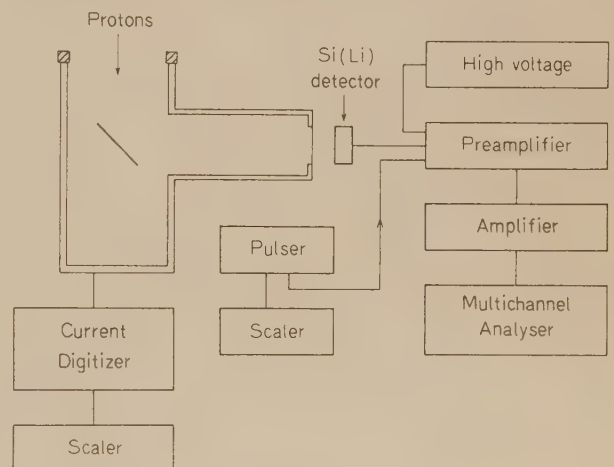


Fig. 3. The detector set-up and electronics

C. Targets

All targets were self-supporting foils. They covered a 9 mm diameter hole in a frame made of ultra-pure aluminum. The purity of the foils was better than 99.9% (99.7% for Ti) according to the manufacturer. No impurity peaks contributing more than 1% to the total mass of the foils were observed in the x-ray spectra. The weights of the foils were determined gravimetrically using a micro-balance. The foil sizes were measured with a precision ruler, which was photographed together with the foil and enlarged to give a good reading. A foil to be photographed was placed on a metal plate with a polyethylene sheet inserted in between. Keeping the plate on a few hundred volts allowed electrostatic forces to be used for smoothing the foil. This procedure reduced the error in the target thickness values to between 0.5 and 3% for all foils. Microscopic inhomogeneities in the foils were not studied, but this is not considered to be important, since the uniform beam covers a substantial part of the weighed foils. In the Lund experiments the homogeneous beam profile at the foils was achieved by a beam-sweeping arrangement [13] and in the Uppsala experiments a satisfactorily homogeneous beam profile was obtained as the last focussing magnets were placed about 8 m from the collimator arrangement.

D. Spectrum Analysis

The spectra were analysed on the Univac 1108 computer in Lund using the program SAMPO [19]. This program fits gaussians with exponential tails together

with a background to the spectrum. The peak areas given by the computer were checked for some spectra by hand calculation. For the error estimates, 0.6% error in the peak area was adopted, which is slightly above the one standard deviation statistical error.

E. Deadtime Measurements

A 50 Hz precision pulser coupled through the pre-amplifier made it possible to correct for deadtime losses. Counting rates were kept low, e.g., in the Uppsala experiments, the deadtime correction was of the order of 1%. In the Lund experiments, the sweeping arrangement was used. The beam was then regarded as being well-focussed and the fraction of the analyzing time the beam was actually on the target was estimated by eye from the quartz collimator. The deadtime correction took this timeloss into consideration. The beam was on the target typically 50% of the time and the deadtime correction was generally 1–2%. However, the estimates of the time on target introduced an error in the deadtime correction, which contributes about 0.7% to the total error.

Results and Discussion

A. Cross-Sections

K x-ray production cross-sections were measured for several elements ranging from Ti ($Z=22$) to Ag ($Z=47$) and L x-ray production cross-sections for Au and Pb ($Z=79$ and 82 resp.) using proton energies in the energy interval 1.5–11 MeV. For most elements and

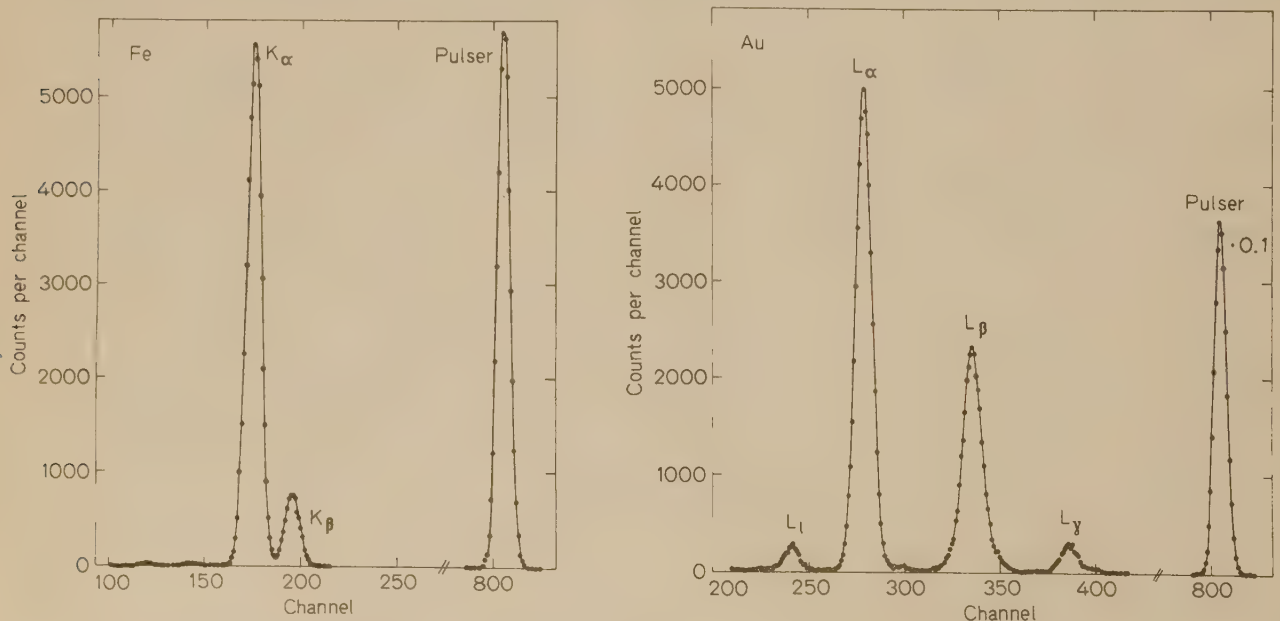


Fig. 4a and b. K x-ray spectrum from iron and L x-ray spectrum from gold

Table 2. Experimental K x-ray production cross-sections, σ_p , and ionization cross-section, σ_i , using fluorescence yields from Ref. [20]. $\bar{\sigma}_i$ are mean values of the ionization cross-sections when measured in two runs. Errors corresponding to one standard deviation are given in percent

Ti, Z=22, $\omega=0.219\pm0.018$					Fe, Z=26, $\omega=0.347\pm0.008$					Co, Z=27, $\omega=0.381\pm0.027$				
E_p MeV	foil ^a	σ_p barn	σ_i barn	$\bar{\sigma}_i$ barn	E_p MeV	foil ^a	σ_p barn	σ_i barn	$\bar{\sigma}_i$ barn	E_p MeV	foil ^a	σ_p barn	σ_i barn	$\bar{\sigma}_i$ barn
1.50	2	132	603	597	1.50	2	47.3	136	135	1.50	2	37.2	97.5	184
1.50	1	129	590		1.50	1	46.2	133		2.00	2	70.2	184	
2.00	2	218	996	983	2.00	2	87.6	252	250	2.50	2	109	286	384
2.00	1	212	970		2.00	1	85.6	247		3.00	2	146	384	
2.50	2	315	1440	1420	2.50	2	135	390	381	4.96	1	267	700	959
2.50	1	308	1410		2.50	1	128	368		5.96	1	320	840	
3.00	2	383	1750	3230	3.00	2	175	504	1250	6.94	1	366	961	1110
4.96	1	582	2660		4.97	1	324	933		6.96	1	364	956	
5.96	1	650	2970	3410	5.96	1	388	1120	1430	8.94	1	422	1110	1210
6.96	1	713	3260		6.94	1	439	1260		8.94	1	428	1120	
6.96	1	703	3210	3480	6.96	1	432	1240	1520	10.93	1	463	1210	
8.94	1	749	3420		8.94	1	491	1410		10.93	1	460	1210	
8.94	1	747	3410		8.94	1	499	1440						
10.93	1	767	3500		10.93	1	525	1510						
10.93	1	758	3460		10.93	1	533	1540						
Error (%)		7.5	11	11	Error (%)		5	5.5	5	Error (%)		4.5	8.5	8.5
^a foil 1 1.976 ± 0.059 mg/cm ² foil 2 1.906 ± 0.019 mg/cm ²					^a foil 1 1.033 ± 0.031 mg/cm ² foil 3 0.965 ± 0.007 mg/cm ²					^a foil 1 0.920 ± 0.028 mg/cm ² foil 2 0.882 ± 0.006 mg/cm ²				

Ni, Z=28, $\omega=0.414\pm0.028$					Cu, Z=29, $\omega=0.445\pm0.009$					Ag, Z=47, $\omega=0.830\pm0.025$				
E_p MeV	foil ^a	σ_p barn	σ_i barn	$\bar{\sigma}_i$ barn	E_p MeV	foil ^a	σ_p barn	σ_i barn	$\bar{\sigma}_i$ barn	E_p MeV	foil ^a	σ_p barn	σ_i barn	$\bar{\sigma}_i$ barn
1.50	1	26.6	64.2	66.6	1.50	1	21.3	47.8	48.2	1.50	1	0.282	0.340	0.344
1.50	2	28.3	68.5		1.50	2	21.6	48.6		1.50	2	0.288	0.348	
2.00	1	53.2	129	134	2.00	1	42.4	95.3	96.0	2.00	1	0.739	0.890	0.907
2.00	2	57.3	138		2.00	2	43.0	96.7		2.00	2	0.765	0.922	
2.50	1	84.5	204	209	2.50	1	68.1	153	154	2.50	1	1.43	1.72	1.73
2.50	2	88.2	213		2.50	2	69.3	156		2.50	2	1.44	1.74	
2.98	1	114	274	284	3.00	2	95.1	214	667	2.98	1	2.19	2.64	2.78
3.00	2	120	291		4.96	1	206	463		3.00	2	2.42	2.92	
4.97	1	233	562	778	5.96	1	252	566	797	4.97	1	7.68	9.25	18.2
5.96	1	282	680		6.96	1	301	673		5.96	1	11.2	13.5	
6.94	1	321	776	926	6.96	1	293	658	894	6.94	1	15.4	18.5	28.4
6.95	1	323	781		8.94	1	352	790		6.96	1	14.8	17.9	
8.94	1	384	927	1010	8.94	1	357	803		8.94	1	23.8	28.7	38.8
8.94	1	383	926		10.93	1	397	892		8.94	1	23.4	28.2	
10.93	1	420	1020		10.93	1	399	897		10.93	1	32.1	38.7	
10.93	1	414	1000							10.93	1	32.2	38.8	
Error (%)		4.5	8	8	Error (%)		4	4.5	4.5	Error (%)		3.5	4.5	4.5
^a foil 1 0.794 ± 0.024 mg/cm ² foil 2 0.787 ± 0.006 mg/cm ²					^a foil 1 1.162 ± 0.020 mg/cm ² foil 2 1.151 ± 0.012 mg/cm ²					^a foil 1 1.280 ± 0.026 mg/cm ² foil 2 1.243 ± 0.010 mg/cm ²				

proton energies, the measurements were performed twice and, for the lower energies, two foils of every element were used. All measurements on one element at a certain energy agreed within the experimental errors. Reproducibility was checked in several cases and the results were compatible with statistics. Fig. 4

shows typical spectra from a couple of the elements. The spectra did not deteriorate at higher proton energies. Tables 2 and 3 contain data on the foils used, the x-ray production cross-section and the fluorescence yield used to calculate the ionization cross-section. For L x-rays, no ionization cross-sections are given.

Table 3. Experimental L x-ray production cross-sections, σ_p , $\bar{\sigma}_p$ are mean values of the production cross-sections for proton energies for which two or three measurements have been performed. Errors corresponding to one standard deviation are given in percent

Au, Z = 79				Pb, Z = 82			
E_p MeV	foil ^a	σ_p barn	$\bar{\sigma}_p$ barn	E_p MeV	foil ^a	σ_p barn	$\bar{\sigma}_p$ barn
1.50	1	14.8	14.5	1.50	1	10.6	
1.50	1	14.4		2.00	1	24.3	
1.50	2	14.4	54.0	2.50	1	35.9	
2.00	2	30.7		3.00	1	51.7	
2.50	1	53.6		4.97	1	130	
2.50	2	54.4		5.96	1	174	
3.00	2	77.4	179	6.96	1	214	212
4.97	1	178		6.96	1	209	
4.97	1	179	279	8.94	1	285	287
5.97	1	236		8.94	1	288	
6.96	1	284	374	10.93	1	350	350
6.96	1	274		10.93	1	349	
8.94	1	371	451				
8.94	1	377					
10.93	1	454					
10.93	1	448					
Error (%)	3	3		Error (%)	3	3	

^a foil 1 2.304 ± 0.016 mg/cm²
foil 2 2.917 ± 0.023 mg/cm².

^a foil 1 1.140 ± 0.015 mg/cm²

due to the complex nature of the spectra and the poor resolution of the detector.

In Fig. 5 the ionization cross-sections for K shell and production cross-sections for L x-rays are plotted as a function of proton energy. As is evident from the figures, the comparable experimental results in this work agree satisfactorily with the results of Refs. [4, 5, 21].

The x-ray emission is assumed to be isotropic [22]. The x-ray production cross-sections, in cm², were calculated from the formula.

$$\sigma_{\text{prod}} = \frac{SA}{N_0 n a} \cdot \frac{4\pi r^2}{y} \cdot \frac{1}{t} \cdot \frac{1}{\varepsilon} \cdot D \cdot \frac{1}{b},$$

where

S number of counts in corresponding peaks,

N_0 Avogadro's number = $6.022 \cdot 10^{23}$ atoms per gram mole,

r distance target-detector (cm),

D deadtime correction factor,

A atomic weight of the target element (u),

n number of protons passing through the target,

a effective target thickness (g/cm²),

y detector area = 0.2599 cm²,

t a factor correcting for the proton slowing down in the target and the x-ray absorption in the target,

ε detector efficiency and

b correction factor for x-ray absorption in air.

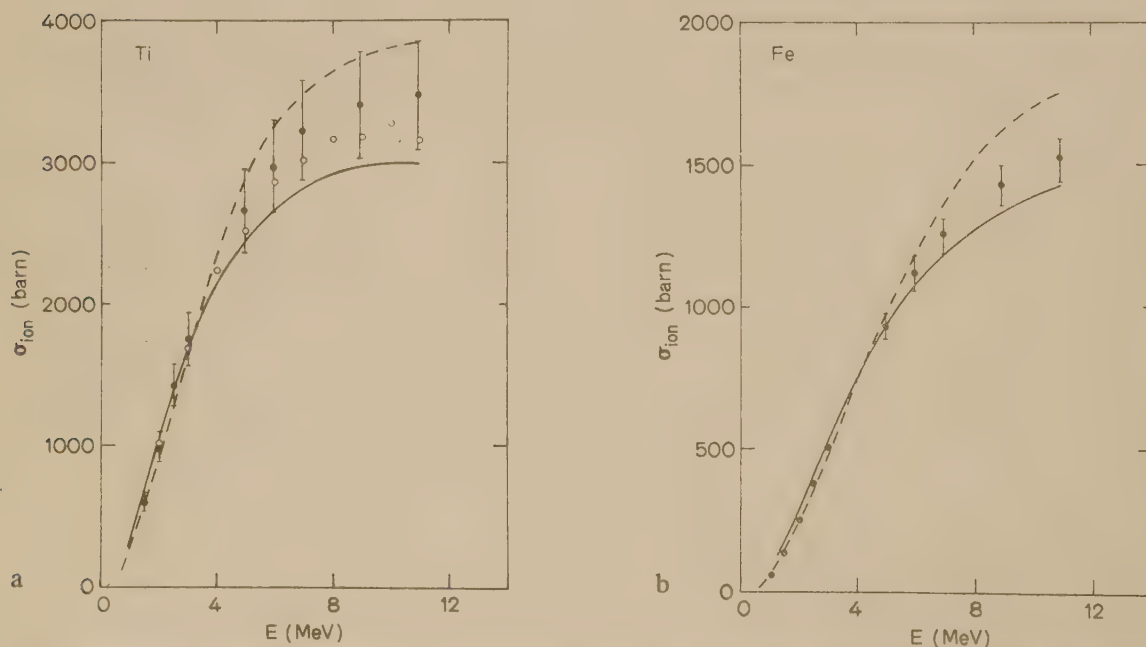


Fig. 5a-h. K -ionization cross-sections for Ti, Fe, Co, Ni, Cu and Ag and L -production cross-sections for Au and Pb. The solid curves are PWBA-calculations and the dashed curves BEA-calculations. The circles are experimental values from other authors. For Ti and Ni [4] the uncertainties are between 11 and 13%, for Ag [5] 20% and for Au and Pb [21] 20%. The values from Refs. [4] and [5] have been recalculated using the fluorescence yields given in Table 2

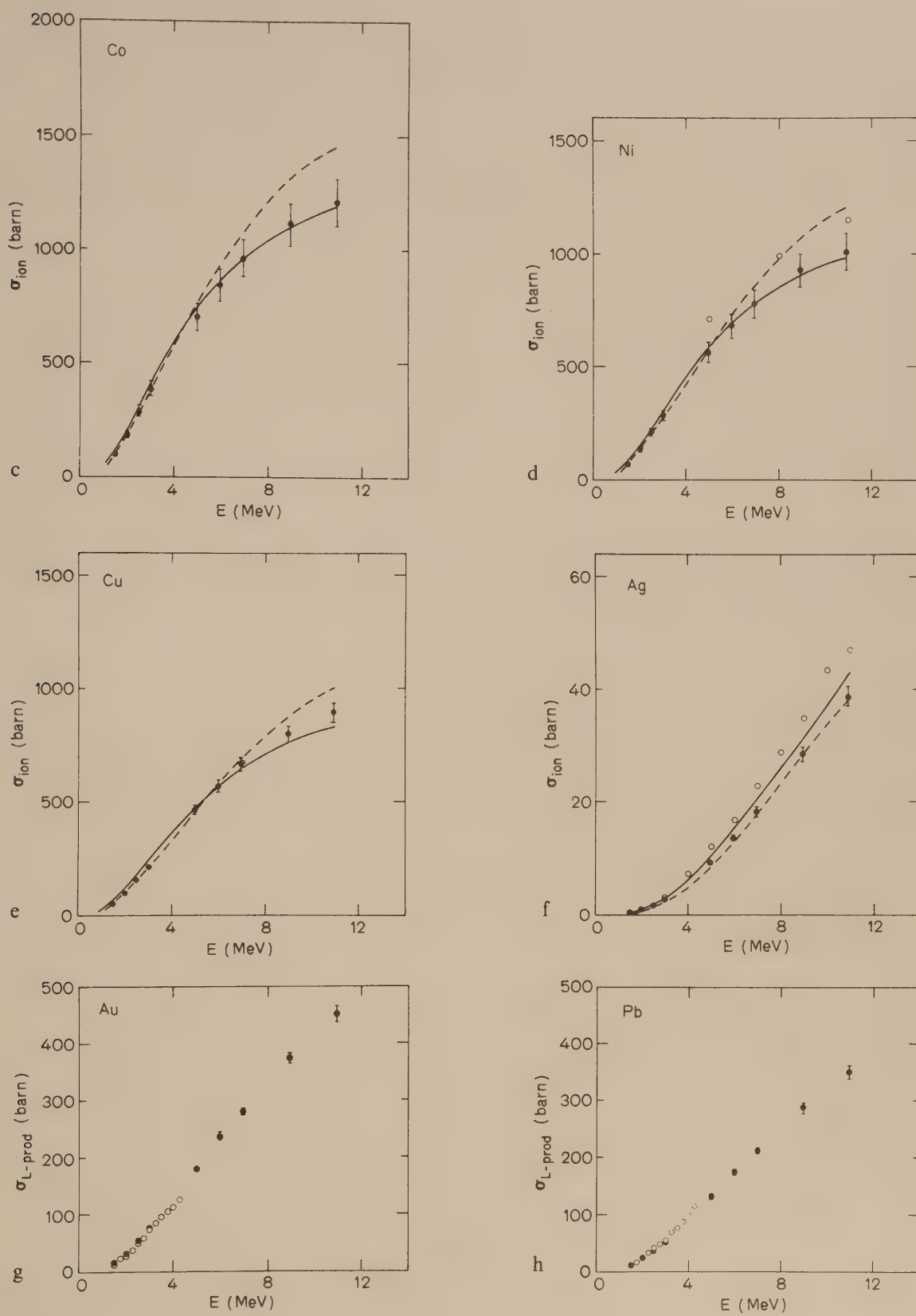


Fig. 5c-h

The ionization cross-section is then obtained by dividing with the fluorescence yield ω_K ,

$$\sigma_{\text{ion}} = \sigma_{\text{prod}} / \omega_K.$$

The deadtime correction factor is calculated from the formula,

$$D = VP / (R - (1 - V)P)$$

where

V fraction of time the beam is on the target,

P number of pulses from the pulser registered on the scaler and

R number of counts in the pulser peak in the spectrum.

The target correction factor is calculated by integrating over the target thickness, a :

$$t = \frac{\int_0^a \sigma(x) e^{-\mu x} dx}{\sigma(0) \cdot a},$$

where

σ x-ray production cross-section as obtained from the PWBA formula (see below) and

μ x-ray absorption coefficient (from Storm *et al.* [23]).

The factor t is typically 0.85 and always in the interval 0.72 to 0.99.

To calculate t the shape of the cross-section curve as given by the PWBA calculations is used. By inserting errors on the values used in the calculations, the error in t was estimated. An error in the shape predicted by PWBA of the order that can be estimated from Fig. 5 does not contribute more than 0.1% to the total error of t . In the evaluation of t , the proton energy at depth x in the target is needed. This is obtained from an integration using stopping powers from Williamson *et al.* [24] and for Ti from Northcliffe and Schilling [25]. The errors given in these tables are included in the total error of the correction factor t . The total error in t is dominated by the 10% error in the x-ray absorption factors from the tables by Storm *et al.* The energy spread of the protons in the target does not contribute to the target correction factor as $\sigma(E)$ is well approximated with a straight line in the proton energy interval involved.

Table 4 summarizes the errors. As can be seen, the main uncertainty comes from the detector efficiency, for which, at low energies, well-known standards are lacking and absorption problems are severe. The values of the fluorescence yields and their errors are included in Tables 2 and 3.

Characteristic x-rays could also be excited by secondary electrons of sufficient energy either directly by

Table 4. Errors in the cross-sections corresponding to an error of one standard deviation in some parameters

Source of error	Error in cross-sections (%)
Peak area (statistical and area determination)	0.6
Current integration	1.0
Target thickness (incl. target angle)	0.5–3.0
Target-detector distance	0.1–0.3
Dead-time correction	0.7
Detector efficiency	2–5
Air absorption	0.01–0.8
Target thickness correction, t	1–4
Proton energy	0.1–1

Table 5. Upper limits of secondary cross-sections using the thick target approximation

E (MeV)	Secondary K -ionization cross-section in percent of σ_i from Table 2						Secondary L -production cross-section in percent of σ_p from Table 3	
	Ti	Fe	Co	Ni	Cu	Ag	Au	Pb
2.5	0	0	0	0	0	0	0	0
3	0.5	0	0	0	0	0	0	0
5	2.5	1	0.5	0	0	0	0	0
7	4	2.5	2	1.5	0	0	0	0
9	5	3.5	3	2.5	2	0	2.5	0.5
11	6	4	4	3.5	3	0	4	1.5

collisions or indirectly by the bremsstrahlung associated with them. Following Jarvis *et al.* [6, 26], calculations were performed in the thick target approximation, in which all the secondary electrons are supposed to stop in the foil. The electrons of interest are assumed to be emitted in the forward direction. The results are shown in Table 5. However, the thick target approximation gives too high values for the foil thickness used in this experiment, especially for protons of the higher energies, since according to the Thomas-Whiddington Energy-Loss Equation [27], a 20 keV electron penetrating a 1 mg/cm² thick foil loses on the average about 9.5 keV. Hence, the calculated contributions from the secondary ionization are only upper limits. They are mostly well within the errors quoted in Tables 2 and 3. However, for 11 MeV protons on gold the upper limit of the contribution from secondary ionization is as large as 4%.

B. Comparisons with Theory

To compare experimental and theoretical K ionization cross-sections, the predictions of PWBA and BEA have been included in Fig. 5. The PWBA values have been calculated using formulas from Ref. [1] and tables in Ref. [28]. The predictions of the binary-encounter

approximation were calculated by scaling as suggested by Garcia [3], using his values of Mg cross-sections.

Comparison between the PWBA and BEA predictions and the experimental results shows that PWBA is quite good at higher energies and that BEA is as good at lower energies. In both cases, the discrepancies are of the order of the experimental error. At lower energies, PWBA gives values that are 10–15% too high. At higher energies, BEA gives values that are 10–20% too high.

Comparison between experiment and theory in the L x-ray production experiments is more complex owing to the rather low resolution of the detector used, the occurrence of Coster-Krönig transitions and the different values of fluorescence yields in the different subshells. As is discussed below, the ionization of the three subshells depends on the proton energy, making the use of a mean fluorescence yield value dubious. However, as the L_{α} - and L_{β} -lines arise only by transitions to the L_3 shell, a comparison with the binary-encounter model, using values of Coster-Krönig and fluorescence yields from the literature, and our experiments can be performed in the following way: According to Bambynek *et al.* [20], the number of vacancies in the L_3 shell is given by

$$V_3 = N_3 + N_2 f_{23} + N_1 (f_{13} + f_{12} f_{23}),$$

where

V_3 is the number of vacancies in subshell 3,

N_r is the predicted number of vacancies per atom in the r shell as computed by scaling from the binary-encounter theory and

f_{ij} is the Coster-Krönig transition coefficient for a transition from subshell i to subshell j .

By multiplying V_3 with the fluorescence yield ω_3 and using a correction factor to take into account the fact that some L_3 vacancies are filled by t , s , β_2 , β_5 , β_6 , β_7 , or β_{15} -transitions, a number is obtained which may be compared with the sum of the experimental L_{α} and L_{β} x-ray production cross-sections. Values of 0.83 for Au and 0.82 for Pb are determined for these correction factors, using values of relative intensities given in Ref. [23]. This assumes that, given a vacancy in the L_3 shell, the relative transition probabilities are independent of how the vacancy was created. The ω_3 and f_{ij} values are taken from Ref. [20], using measured values for Pb and theoretical for Au. The comparisons are presented in Fig. 6. The agreement is very good at low proton energies, but at higher energies the calculated values exceed the experimental ones by about 20%.

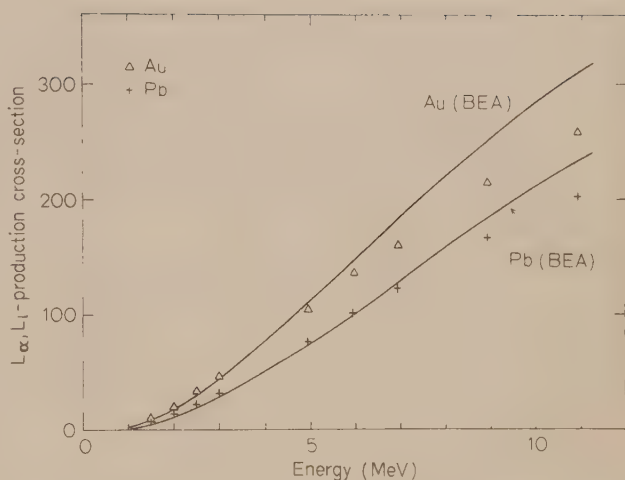


Fig. 6. The sum of the experimental L_{β} - and L_{α} -production cross-sections compared with BEA calculations. Values of the fluorescence yields $\omega_3=0.327$ and $\omega_3=0.315$ for Au and Pb respectively are used. The errors in the experimental points are estimated to 2–3%.

C. Relative x-ray Intensities

The relative intensities of the various x-ray groups following vacancies in the K - or L -shells have been calculated. In Tables 6 and 7 are given values for K_{β}/K_{α} or L_{β}/L_{α} , L_{β}/L_{α} and L_{γ}/L_{α} for the elements used in this work except for Ti, for which the resolution of the detector did not permit a reliable separation of the two components. The K_{β}/K_{α} values are the averages of all the measurements on a certain element and thus include values obtained at the various proton energies. The values agree quite well with those obtained by other groups [5, 16, 17, 29, 30]. The values of the K_{β}/K_{α} ratio as a function of proton energy were checked for any variation with energy. No significant variation of the ratio with the energy was found. For example, a least-squares fitted straight line to the values for Cu has slope $K=0.00008 \pm 0.00013 (\text{MeV})^{-1}$, where the quoted error is two standard deviations.

As can be seen from Table 7 some of the relative L -line intensities are energy dependent. L_{β}/L_{α} and L_{γ}/L_{α} increase with the proton energy, while L_{β}/L_{α} is constant. This latter constancy is expected in view of the fact that both lines are due to transitions to the L_3 shell and multiple ionizations are not expected when protons are used for excitation. The variations in the other two ratios are in qualitative agreement with the predictions of the binary-encounter approximation of relative ionization probabilities as a function of proton energy.

D. An Empirical Expression

To make available a convenient expression for experimental ionization cross-sections, Fig. 7 was prepared.

Table 6. Relative *K* x-ray intensities

<i>Z</i>		<i>I</i> (<i>K_β</i>)/ <i>I</i> (<i>K_α</i>)				
		Proton excitation		Radioisotopes	Photons	
		This work	[5] and [17]	[16]	[29]	[30]
26	Fe	0.1369±0.0035		0.1283±0.0025	0.1366±0.0011	0.136
27	Co	0.1399±0.0025			0.1376±0.0011	
28	Ni	0.1359±0.0018			0.1385±0.0011	
29	Cu	0.1385±0.0018	0.1282±0.0017 [17]		0.1387±0.0011	0.138
47	Ag	0.2123±0.0068	0.214 ±0.015 [5]	0.2110±0.0042		0.219

Table 7. Relative *L* x-ray intensities. Errors corresponding to one standard deviation are given in percent (pe)

	<i>E_p</i> MeV	<i>I</i> (<i>L_i</i>)	pe	<i>I</i> (<i>L_β</i>)	pe	<i>I</i> (<i>L_γ</i>)	pe	<i>I</i> (<i>L_α</i>)	pe
		<i>I</i> (<i>L_α</i>)		<i>I</i> (<i>L_α</i>)		<i>I</i> (<i>L_α</i>)		<i>I</i> (<i>L_{total}</i>)	
Au	1.50	0.0530	1.5	0.545	1	0.0748	1.5	0.598	1
	2.00	0.0493	2.5	0.580	1.5	0.0778	2	0.586	1
	2.50	0.0507	2	0.593	1	0.0854	1.5	0.579	1
	3.00	0.0510	2.5	0.611	1.5	0.0906	2	0.571	1
	4.97	0.0465	2	0.648	1	0.104	1.5	0.556	1
	5.97	0.0482	2	0.662	1	0.104	1.5	0.551	1
	6.96	0.0452	1.5	0.664	1	0.111	1.5	0.549	1
	8.94	0.0484	1.5	0.666	1	0.110	1.5	0.548	1
	10.93	0.0477	1.5	0.676	1	0.106	1.5	0.547	1
Pb	1.50	0.0556	3	0.546	1.5	0.0744	2.5	0.596	1
	2.00	0.0529	2.5	0.566	1.5	0.0819	2	0.588	1
	2.50	0.0536	2.5	0.579	1.5	0.0835	2	0.583	1
	3.00	0.0529	3	0.602	1.5	0.0878	2	0.574	1
	4.97	0.0517	2	0.636	1.5	0.101	2	0.559	1
	5.96	0.0512	2.5	0.646	1.5	0.105	2	0.555	1
	6.96	0.0493	1.5	0.650	1	0.108	1.5	0.553	1
	8.94	0.0515	1.5	0.653	1	0.107	1.5	0.552	1
	10.93	0.0521	1.5	0.654	1	0.110	1.5	0.551	1

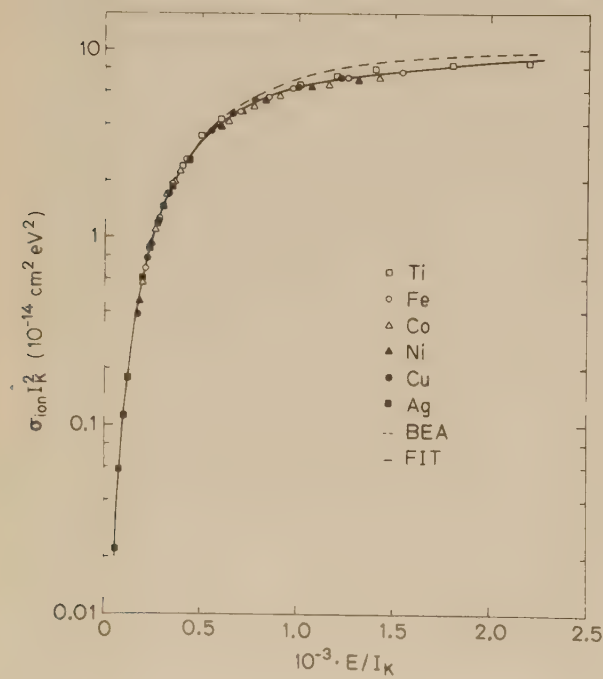


Fig. 7. The empirical curve compared with experimental points and the binary-encounter approximation

The curve is

$$\epsilon \log(\sigma_{\text{ion}} I_k^2) = \sum_{i=0}^5 b_i x^i \quad -3.0 \leq x \leq 0.8,$$

where

$$b_0 = 1.8451 \quad b_3 = 0.17481$$

$$b_1 = 0.60365 \quad b_4 = 0.11142$$

$$b_2 = -0.44481 \quad b_5 = 0.01941$$

and $x = \epsilon \log(10^{-3} E/I_k)$. I_k is the ionization energy in eV and E is the proton energy in eV. The expression is very useful for computer evaluation of results, especially if thick targets are used. The unit of the ionization cross-section is 10^{-14} cm^2 .

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ELEMENTAL TRACE ANALYSIS OF SMALL SAMPLES BY

PROTON INDUCED X-RAY EMISSION

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ABSTRACT:

Proton induced X-ray emission (PIXE) has been developed for quantitative analysis of 12-15 elements simultaneously in small nonhomogeneous samples such as impactor collected aerosol size fractions using a low energy (3.7 MeV) proton beam from a Van de Graaff generator. The procedure is described in detail as are numerous tests of the performance of the system and the analytical methodology. Detection limits in a 10 min run are in the 10^{-9} g range. The standard deviation amounts to 6 % for the set-up and to 15 % for the total analytical procedure. The method is absolute as standards are used only to check the stability of the system.

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INTRODUCTION

Present environmental concerns have been a major impetus to efforts towards ultra-sensitive, multi-element analysis procedures, capable of ready application to environmental and biological samples. The rapidly expanding scientific literature on X-ray emission analysis illustrates that this technique has become an increasingly important tool for elemental analysis, especially since Si(Li) detectors were introduced a few years ago. Although energy-dispersive X-ray fluorescence, like any other available technique, cannot measure all elements of interest in the concentration ranges of environmental samples, it has the potential of providing the rapid, non-destructive, low-cost, multi-element analysis capability, required to investigate and monitor the behaviour of many interesting elements in various matrices.

It is generally recognized that the applicability of radio-isotope induced X-ray fluorescence is limited by its relative low sensitivity. Since important progress has been achieved in the design and characteristics of X-ray tubes and the associated semi-conductor detectors and electronics, X-ray excitation using X-ray tubes allows competitive trace element analysis (1).

X-ray emission by charges particle excitation offers an other attractive alternative. In 1970, the potential of heavy charged particles as an excitation source was recognized and an interference-free sensitivity down to the picogram range demonstrated (2).

The excellent capability of accelerator beams for X-ray emission analysis is partially due to the very low background radiation associated with the excitation: the main contribution being Bremsstrahlung from secondary electrons in the target. This low energy background can also be dealt with more easily than the high-energy background from the scattering in the sample of exciting X-rays from a tube or a radioisotope source or the continuous background from electron excitation. The very high intensity of ionizing radiation fluxes obtainable from accelerators also contributes substantially to the power of the method.

The capability of high-energy α -particles as a source for X-ray excitation was investigated by Watson et al (3), Flocchini et al (4) and Perry and Brady (5); in a comparative study conducted by Cooper (6) it was found to be less attractive than X-ray induced X-ray fluorescence using modern X-ray tubes. Low energy proton induced X-ray emission, however, seems to offer distinct advantages whenever high sensitivities are required and/or small sized samples are to be analysed.

Recently, Gilfrich et al (7) compared several approaches to X-ray elemental analysis and found that proton excitation offers the highest sensitivity. Folkman et al (8) and Herman et al (9) discussed the optimum choice of heavy particle and beam energy. They concluded that protons of a few MeV energy provide the preferable combination for high sensitivity analysis. As there are a large number of accelerators available that are capable of delivering such beams, the prospects for rapid development of the field are bright.

The present work describes an apparatus set-up, designed for proton induced X-ray emission analysis, and discusses the methodology of the analytical procedure. It presents a thorough evaluation of the performances of both the system and the technique, and a multiple check of the quantitative character of the results, especially with respect to aerosol analysis.

Proton induced X-ray emission analysis (PIXE) has been used in feasibility studies by e.g. Johansson et al (10), Lochmüller et al (11), Campbell et al (12), Rudolph et al (13) and others and is currently applied to the analysis of, i.a., aerosols by Cahill and Feeney (14), Van Grieken et al (15) and Johansson et al (16, 17), to zircon minerals by Van Grieken et al (18) and to thick samples such as steel slabs or teeth by, e.g. Ahlberg et al (19).

EXPERIMENTAL PROCEDURES

When a sample is bombarded by charged particles, e.g. a proton beam, inner shell electrons are ejected and characteristic X-rays emitted when the excited atoms return to their ground states. By determining the energy and intensity of the X-rays, specific

quantitative analyses can be performed.

Samples to be analysed are applied on thin foils ($\sim 40 \mu\text{g}/\text{cm}^2$) of polystyrene, either by being directly collected on these foils, as in the aerosol analysis program, or transferred to them. Solutions, e.g. can be spotted with a pipet and, after evaporation, the residue can be analysed directly provided care is taken to avoid absorption problems. Polystyrene is easy to handle and has a considerable strength. It also withstands sufficient beam intensities to allow count-rate limited analysis.

The carrier foils are prepared from a 4 % solution of polystyrene in benzene. Microscope slides previously coated with NaOH are inserted and then withdrawn at a constant rate of several cm/s. After evaporation of the benzene, the polystyrene coating can be cut to suitable pieces (e.g. 1 cm^2), then floated off by obliquely lowering the glass slide into distilled water. The foils are then easily picked up on an aluminum frame with an ellipsoidal hole. The whole target preparation procedure is performed in a dust free laminar flow work station to reduce contamination. Eight frames with samples are mounted together on a rod, held in a barrel that, when closed, shields the targets from airborne contaminants during the transportation to the irradiation site. The foils generally have low blank values. In 33 blank foils, Ca was detected in 28 foils with an average of 3.4 ng Ca per foil in the beam, Cl in 20 foils (4.8 ng), S in 16 (4.6 ng), Mn and Fe in 11 (2 ng) and Zn in 11 (14 ng). Occasionally, small amounts of Ti, Cu and Pb were present. It is advisable to analyse blank foils whenever these elements should be determined near the detection limit.

The irradiation chamber (Figure 1) at the end of the accelerator beam line is described in detail in ref. 20. The barrel fits into a special slot in the chamber. Targets can be positioned and barrels can be exchanged without breaking the accelerator vacuum. The 4.5 mm beam focused through a set of carbon collimators, transverses the thin target and is dumped into a Faraday cup connected to a beam integrator. Relative to the beam direction the target is generally

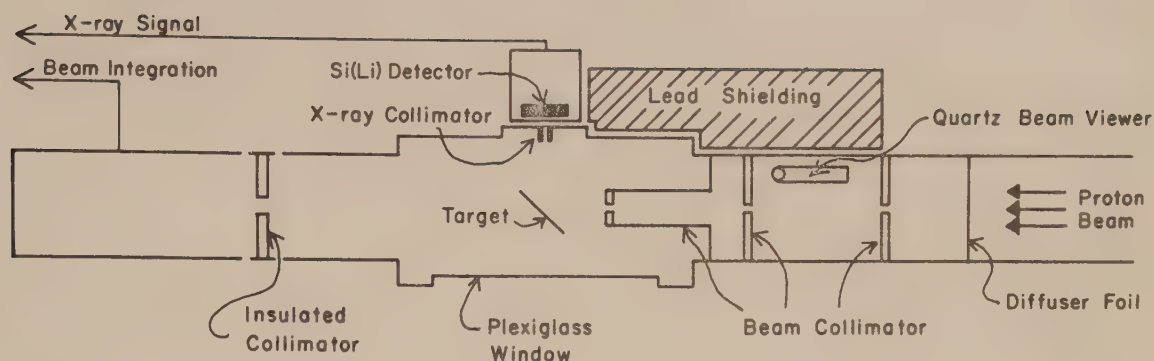


Figure 1. Irradiation chamber.

orientated in 45° and the X-ray detector in 90° . As the analysis of heterogeneous samples assumes a uniform beam hitting the target (10), a diffuser foil (21) is inserted upstream from the collimators. The thickness of the Al foil used as a diffuser ($\sim 5 \text{ mg/cm}^2$) and the distance between the foil and last collimator ($\sim 1 \text{ m}$) have been chosen to ensure uniform sample irradiation. Using a tiny piece of Zr as a probe (22), we have mapped the horizontal and vertical beam profile for different diffuser arrangements. One typical diameter for the final set-up, as shown in Figure 2, demonstrates the beam intensity to be homogeneous to about 5 %, quite satisfactory for trace element determinations. The sample holding rods can easily be moved vertically and horizontally to ensure that small heterogeneous samples, such as aerosol deposits from a single-orifice impactor, are completely enveloped by the beam. In the case of large homogeneous samples, the positioning facilities are only manipulated to make sure that no beam hits the frame on which the sample is suspended.

A lithium-drifted silicon detector is used for X-ray detection. The detector has a sensitive depth of 5 mm, an area of 80 mm^2 and a resolution of 180 eV at 5.9 keV (FWHM). Figure 3 shows a typical X-ray spectrum recorded during an irradiation in our aerosol analysis

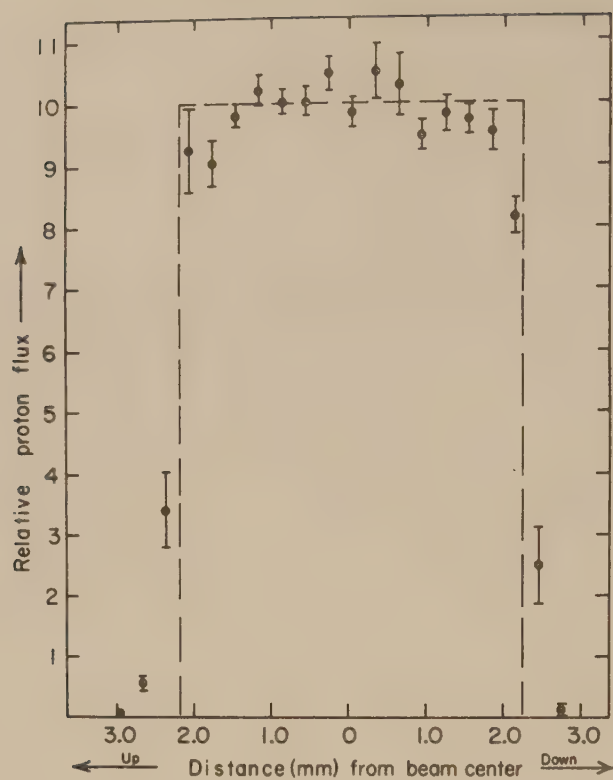


Figure 2. Proton beam intensity measured along a beam diameter.

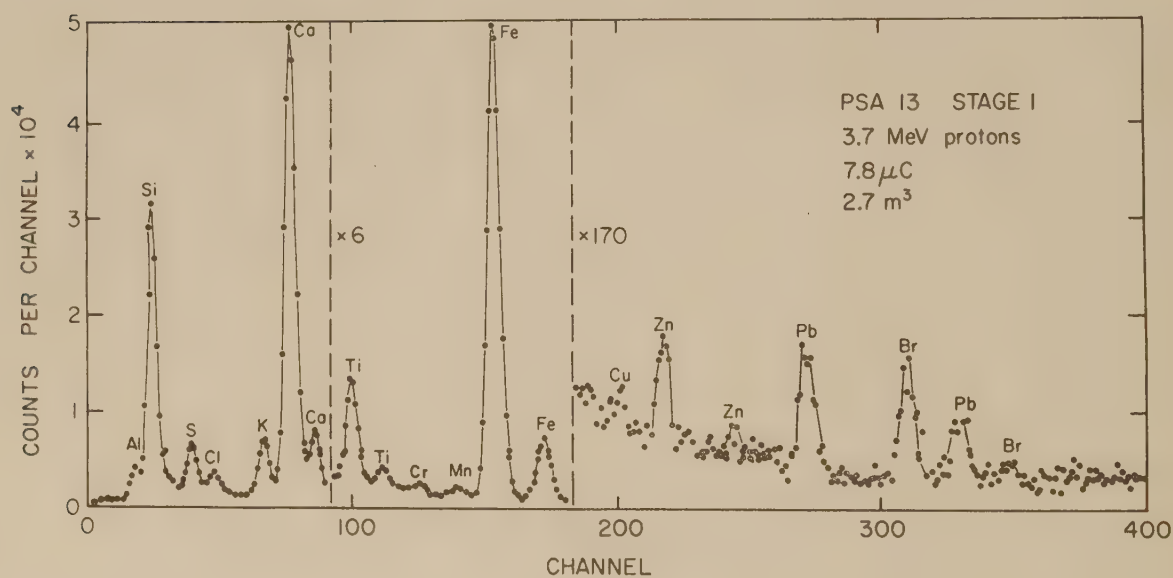


Figure 3. X-ray spectrum obtained by proton irradiation of an impactor-collected aerosol sample.

program. Increasing channel numbers along the X-axis correspond linearly to increasing X-ray energy.

The weight in grams, G , of an element is given by

$$G = \frac{N \cdot W_a}{n \cdot \sigma_p \cdot (\Omega/4\pi) \epsilon \cdot t \cdot A} \quad (1)$$

where N represents the number of counts in a corresponding peak, n the number of protons per cm^2 , σ_p the X-ray production cross section, Ω the solid angle subtended by the collimator in front of the detector, ϵ the detector efficiency including absorption losses in windows between the target and the detector, t the fraction of the produced X-rays that escapes absorption in the target in the direction of the detector. A is Avogadro's number and W_a the atomic weight of the element.

The proton flux, n , is obtained by dividing the integrated beam current for each run by the beam area.

The number of counts in the peaks in the X-ray spectrum is evaluated by fitting a Gaussian with exponential tails to each peak together with a polynomial background that extends over the total interval used in the fitting procedure. Up to 6 peaks can be fitted together in a standard code called SAMPO (23). A smaller and faster code such as recently developed by Harrisson and Eldred (24) for particle induced X-ray spectrum analysis, would be advantageous for routine operation.

The X-ray production cross sections in equation (1) are obtained from an empirical expression for inner shell ionization, σ_{ion} (25). The X-ray production cross section is then calculated from

$$\sigma_p = \sigma_{\text{ion}} \omega_k \quad (2)$$

where ω is the fluorescence yield and k the relative intensity of the peak used in the calculation. Values of ω and k are obtained from ref. 26. σ_p depends on the energy of the protons. For proton energies below 1 MeV, σ_p varies approximately proportional to E_p^4 (27), while for increasing energies a maximum is reached at about 20 MeV for Z around 30. The background, on the other hand, increases with increasing proton energy giving an optimal proton energy for high sensitivity analysis of a few MeV, varying with Z of the element (8, 9). For this investigation a 4.3 MeV proton beam was chosen: this is the lowest conveniently available energy from Florida State University's Super FN Tandem accelerator. After passing through the diffuser foil, the beam energy was reduced to 3.7 MeV and some energy spread introduced by straggling. The effect of the energy spread on the effective σ_p introduces an analytical error of less than 0.5 %.

The solid angle subtended by the detector is calculated from the area of the circular 6 mm collimator in front of the detector and its distance, 10 cm, to the target. The location of the detector is fixed by the use of a specially designed sleeve which slips over the tube on the irradiation chamber which extends towards the detector and over the detector housing. Inside this sleeve the collimator and suitable absorbers, if needed, are located.

The detector efficiency is of primary importance for accurate quantitative analysis by equation (1). Efficiency curves provided by manufacturers are generally calculated from X-ray absorption coefficients. This is only a rough estimate of the true efficiency as shown in e.g. ref. 28. Also we want to include the window on the irradiation chamber in the efficiency curve. Experimental efficiency determinations are generally done utilizing carefully calibrated radioactive sources. Unfortunately there are no suitable sources giving energies below about 6 keV, a region with strong X-ray absorption and of great interest in elemental analysis. However, equation (1) can be used to determine ϵ if the amount of an element is known. By using thin metal foils ($\sim 50 \mu\text{g}/\text{cm}^2 \pm 5\%$) evaporated on Mylar (29), the efficiency curve in Figure 4 was

determined.

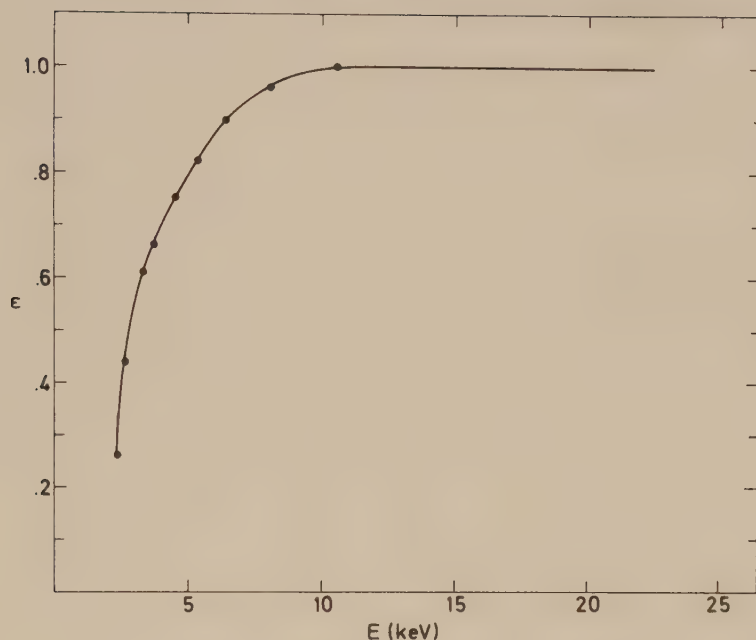


Figure 4. Detector efficiency. The points are experimentally determined.

For quantitative analysis it is preferable to use thin targets, as in this case no corrections for X-ray absorption in the target or for the influence of the proton energy loss on the X-ray production cross sections have to be made. This is generally equivalent to keeping the target thickness below 1 mg/cm^2 . In many practical situations this cannot be fully achieved. For target thicknesses not too much above the thin target criterium, the correction is easily made by using a mean proton energy in the calculations, then taking advantage of the slow variation of the cross sections with proton energy. The X-ray absorption is corrected for by integration in a model where uniform X-ray production is assumed and the sample is approximated with a box.

The correction is then

$$t = \frac{1}{\mu a} (1 - e^{-\mu a}) \quad (3)$$

where a is the target thickness in g/cm^2 and μ the mass absorption coefficient.

RESULTS AND DISCUSSION

The high sensitivity, multi-element analytical method presented has been carefully tested in preparation for routine analytical work.

The linearity of the X-ray response as a function of the amount of material on the target was investigated in the case of K, Cu, Zn and Br (as BrO_3^-) using Y as an internal standard. The targets were prepared from stock solutions by micropipetting onto a polystyrene foil. After evaporation of the solvent the sample is ready for irradiation. As shown in Figure 5 the linearity is very good over the 4 orders of magnitude investigated, as is expected when thin targets are used and the effects of X-ray absorption or proton energy loss in the target are negligible.

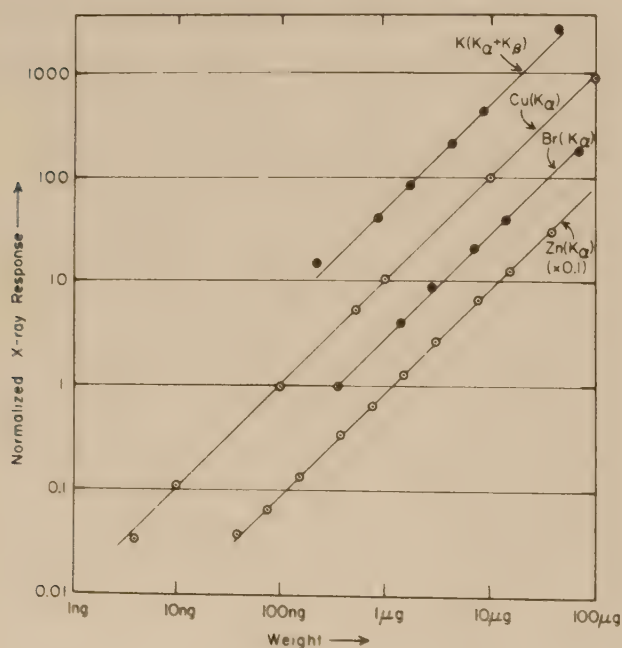


Figure 5. Results from linearity tests.

Inherent in PIXE is the necessity of placing the sample in vacuum with slightly elevated temperatures due to proton energy loss in the sample. To investigate possible volatility losses for some elements in this environment several experiments were conducted. Solutions of As (as AsO_3^{3-} and AsO_4^{3-}), Se (as SeO_3^{2-}), Br (as BrO_3^- and Br^-) and of salts of all metals which are detectable in aerosol samples were prepared with Y as an internal standard. These solutions were spotted on polystyrene foils and analysed after evaporation. The internal standard enabled a check that no rapid, initial loss of a volatile species occurred or that erroneous results were obtained by relying only on the quantitative values for these elements in which case possible mechanical losses are not distinguishable from the volatile losses. In several runs under routine conditions no significant volatile losses were observed (except in the case of Br^-).

In most analyses, great pain is taken to ensure that the targets are thin enough to require only a small absorption correction. In equation (1) the factor t corrects for X-ray absorption in the target. To quantify this condition X-ray absorption has been calculated for homogenous layers of a "typical" rural aerosol deposit of varying total thickness, consisting of 76 % C, 9 % O, 2 % Al, 4.2 % Si, 5 % S, 2.9 % Ca and 0.9 % Fe. X-ray absorption coefficients have been taken from ref. 30. No allowances have been made for particle size effects, occurring when very large particles are present. For low Z elements, e.g. S, the correction is as large as 20 % already for a sample thickness of 1 mg/cm^2 , while higher Z elements, e.g. Cu may be determined in a 20 mg/cm^2 matrix with a 20 % correction, Figure 6.

The protons are slowed down when passing through the target reducing the effective X-ray production cross section. For targets of a few mg/cm^2 thickness, this is an effect on the order of a few per cent and can easily be corrected for. For thicker targets, the varying X-ray production with depth in the sample has to be accounted for by appropriate integration over the energy interval of the protons, see e.g. ref. 19.

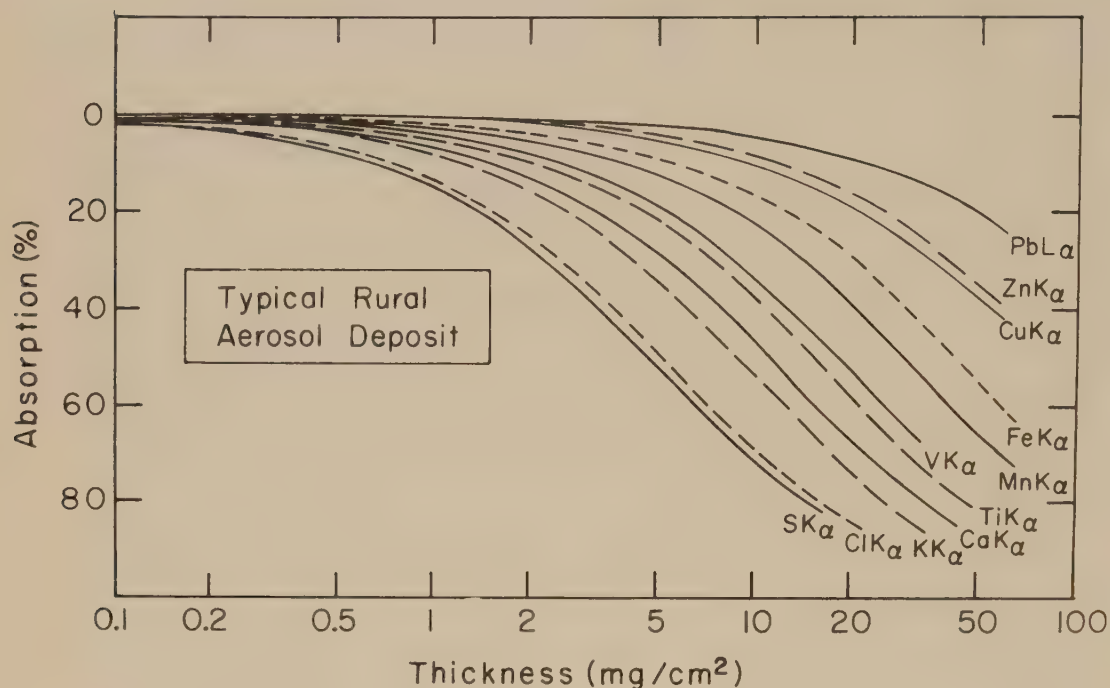


Figure 6. X-ray attenuation in the sample as a function of sample thickness.

Accuracy and precision were investigated in two different ways. The metal foils used for the efficiency determinations of the detector were analysed several times at different accelerator runs over a period of a few months. For most of the standards, two different targets were used. Table 1 presents the data for these experiments. The weighed mean deviation per measurement is 6 %, including contributions from target variations, and all steps of the analytical procedure.

Element (Compound)	Given in μg	P I X E		
		Found in μg	Nr of determ	St dev/meas in %
Cl (NaCl)	6.8	5.6	3	5.2
Cl (KCl)	6.3	6.6	7	6.7
K (KCl)	7.0	7.1	7	6.5
Ca (CaF ₂)	3.7	3.6	5	9.8
Ti	10.2	8.9	3	9.0
Cr	7.2	7.1	5	1.0
Fe	11.5	13.7	5	3.1
Cu (CuS)	7.9	8.1	14	7.1
Ga (GaP)	4.6	4.6	2	7.8
Br (CsBr)	3.1	3.0	3	3.0
Cs (CsBr)	5.2	5.5	3	6.0

Table 1. Results of analysis of thin homogeneous standard samples.

Another test was conducted using the data from all runs with spotted solutions containing known amounts of Mo dissolved as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The "given" amount was 5.5 μg and the mean value of 30 determinations was 5.0 μg with a standard deviation of 15.5 % per measurement calculated from the measurements. The higher standard deviation in this case is, of course, due to the contributions from beam and target inhomogeneity, micropipetting errors, etc. The mean value is 10 % low compared to the given value. This systematical error may be due to an inaccuracy of the pipets or to a small loss of crystallized Mo by flaking off from the target. In several runs other elements were present in the Mo solution. The flaking off explanation is corroborated by the ratios obtained between the elements present in these runs.

A test of the ability to perform quantitative analysis was offered in an inter-laboratory comparison study conducted during the summer of

1973 (31). About a dozen different laboratories participated. X-ray excitation using radioactive sources or different types of X-ray tube excitation, proton and alpha-particle excitation and energy-dispersive as well as wavelength-dispersive detectors were represented. Also neutron activation analysis was done on the samples. All participants analysed Millipore and Whatman 41 filter paper prepared with a known solution containing several elements frequently measured in X-ray analysis. In Table 2 the PIXE results on these samples as well as the gravimetric values are presented. It is clear that our results agree very well with the given values considering our quoted errors. On the whole, the intercomparison study was very successful, with most of the participating laboratories within 10 % of the given values, demonstrating the excellent capabilities of the various methods of X-ray analysis to produce high quality analytical data.

=====				
Spotted on Millipore filter			Spotted on Whatman 41 filter	
	ng added	PIXE result/ gravimetric value	ng added	PIXE result/ gravimetric value
K	2040	1.032	943	.981
V	374	1.071	233	1.069
Mn	1649	1.022	693	.915
Fe	1916	1.093	1269	.988
Cu	300	1.110	202	1.151
As	356	1.154	244	1.120
Pb	813	1.064	558	1.083
MEAN				1.044

Table 2 Results from an interlaboratory comparison study.
The standard deviation on one determination by PIXE
was quoted to be approximately 15 %.

These results demonstrate the capability to provide good data on homogeneous targets. As described above, arrangements were also made to facilitate the analysis of non-homogeneous samples such as samples of particulate matter collected from the atmosphere with a single orifice impactor. Two different experiments were conducted to test the performance of the proposed system on this type of samples.

In the first, thin homogeneous foils of zirconium or aluminium were analysed. Small pieces with carefully determined area ($\sim 1 \text{ mm}^2$) were then cut out of these foils, applied to polystyrene foils with a little starch as a glue and analysed. In the zirconium foils the K-radiation from zirconium was used for the comparison. In the Al case, K-radiation from Fe and Zn impurities were compared to avoid the large correction for X-ray absorption of Al K X-rays in the starch. The results are presented in Table 3.

	Heterogeneous (tiny piece)	Homogeneous foil
Zr-foil	$5.6 \pm .3 \text{ mg/cm}^2$	$5.0 \pm .3 \text{ mg/cm}^2$
Fe in Al-foil	$21.3 \pm 2.6 \text{ } \mu\text{g/cm}^2$	$23.3 \pm 1.9 \text{ } \mu\text{g/cm}^2$
Zn in Al-foil	$1.05 \pm .15 \text{ } \mu\text{g/cm}^2$	$.80 \pm .10 \text{ } \mu\text{g/cm}^2$

Table 3. Comparison between homogeneous and heterogeneous targets.

The second test was offered by the spotted solution used in the accuracy tests discussed above, where heterogeneous residues from spotted solutions were analysed. It is clear from these experiments that small non-homogeneous samples can be accurately analysed. Generally, in X-ray analysis, comparisons are made against specially prepared standards with a composition close to that of the sample being analysed. Good standards are, of course, difficult to prepare for non-homogeneous targets. As we calculate our results directly from physical constants which are accurately known for proton induced X-ray emission and from a few parameters determined for each sample, we have a simplified procedure with extended analytical capability.

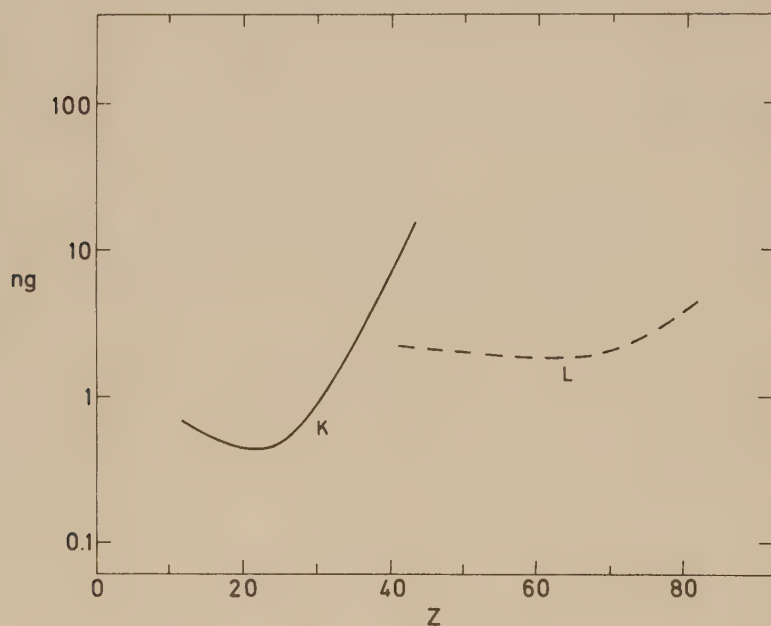


Figure 7. Detection limits in a routine 10 min run.

Figure 7 shows interference-free detection limits obtained in routine analysis of aerosol samples collected by cascade impactor. They have been calculated from the standard criterion $S = 3\sqrt{B}$, where S is the signal required to grant that a peak is significantly above the $2(\text{FWHM})$ background, B . In this calculation equation (1) was used with these routinely used parameters: target collimator

distance 10 cm, detector collimator 0.28 cm^2 , charge $10 \text{ } \mu\text{C}$, corresponding to a beam of $\sim 17 \text{ nA}$ in a 10 min run, beam collimator 0.17 cm^2 . Generally, we have used very low count rates, 500 cps, as the available ADC:s were not capable of maintaining resolution at higher count rates.

Improved, commercially available ADC:s allow considerably higher count rates. The sensitivity for routine operations could thus be improved significantly by simply improving the geometry factor, increasing the beam intensity (polystyrene foils especially when suitable treated withstand μA -beams as do other thin plastics) and absorbing the count rate contribution from low energy Bremsstrahlung to allow full use of the count rate capability in counting informative events. In some applications, e.g. investigations of microstructures, the beam might be reduced to a several μm diameter, resulting in high intensities per area (32).

A homogeneous beam can be obtained not only with the diffuser foils used in this experiment but also with beam sweeping (10). Although quite simple, the diffusers produce the required homogeneity but at the expense of increased beam which must be stopped near the detector and must be shielded against. Beam sweeping on the other hand is more complicated but can easily be coupled with a fast control as used for electron beams (33) in order to correct for deadtime in the analysing equipment. Nuclear reactions in the stopping material give rise to a considerably increased background. When a large amount of beam is needed, the diffusers also have the drawback of reducing the beam intensity with 90-95 %.

Although X-ray analysis is basically very specific in identifying the elements present, the use of energy-dispersive detectors with their rather low energy resolution impairs this capability to some extent, and analysis of a sample with too many elements present above or just above detection limit sometimes offers no unique solution. In the transition region, e.g. the K_α of one element overlap with the K_β of the preceding element, and the ratio between K_α and K_β has to be used in unravelling such interferences. In

cases where only one of the two components is present, the assignment of a peak is sometimes uncertain. The analysis of a spectrum would then improve in quality if some more information was available. A possibility may exist in the application of one or two crystal spectrometers to detect L lines from a few interesting elements.

X-ray analysis can thus be successfully employed for the quantitative analysis of elements with $Z \geq 15$. The limitations for low Z elements are due to increasing X-ray absorption effects in the target. Another approach for the lightest elements showing great promise is the utilization of scattered protons (34). This technique can be applied to the same samples as PIXE and, using solid state charged particle detectors, it is capable of resolving elements of atomic mass ≤ 30 , the combination of the two techniques offers an even more powerful analytical tool.

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ELEMENTAL ABUNDANCE VARIATION WITH PARTICLE SIZE IN NORTH
FLORIDA AEROSOLS.

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ABSTRACT

The variation of elemental abundance with particle size has been determined in aerosols from North Florida sampled near ground by 5-stage cascade impactor in largely unpolluted inland and coastal locations. Dispersion of clay and limestone soil components, sea spray, gas-to-particle conversion reactions, organic processes associated with heavy forest cover, and air pollution by combustion in automotive and stationary sources are important local aerosols sources, and sampling locations were chosen to reflect their varying contributions. The 32 separate size distributions, as determined by proton-induced X-ray emission (PIXE), suggest that Fe and Ti originate mainly from a soil source, distinct from that of Ca which disperses to coarser particles, but K appears to be derived from at least three important sources. Compared with Fe, both Pb and Br are mainly on much finer particles and apparently are both local fuel combustion products, in contrast to Cl, which is found mainly on large particles as expected if it is derived from sea salt. The size distributions of S and Fe, although different, are relatively invariant over all samples collected, except very near the sea coast, suggesting for particulate S mainly a natural terrestrial vapor-to-particle conversion process. Cu, Zn and Mn all show increasing enrichment relative to Fe with decreasing particle size, suggesting source processes involving the vapor phase. The relationships revealed in this model study of a natural atmosphere underlie those of more complex polluted environments.

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INTRODUCTION

Interest in the origin, conversion and eventual fate of particulate matter in the atmosphere has been stimulated by increasing concern about negative effects of air pollution and large-scale monitoring programs are now being considered. Such programs should be designed to yield maximum pollution transport information so as to help regulate emission standards. Relationships among certain pollutants as well as components of the natural background may prove very helpful in this effort (Winchester, 1973).

With the advent of highly precise and sensitive analytical techniques especially by nuclear methods (Dams et al., 1970), detailed study of factors influencing the elemental composition of aerosols has become a practical possibility. Neutron activation results have shown that interelement correlations can be evaluated and source and transport processes can be inferred from high quality analytical data (Dams et al., 1971a, 1971b; John et al., 1973; Rahn, 1971).

Recent advances in analysis by exciting characteristic X-ray emission have led to improvement of sensitivity and speed such that larger numbers of samples taken with cascade impactors over shorter periods can be chemically analyzed and the results numerically intercompared and interpreted. The present model study is a field test of proton-induced X-ray emission (PIXE) analysis with the objective of assessing the value of the method for revealing elemental abundance relationships in a natural environment having both marine and continental air mass regimes but little obvious anthropogenic perturbation.

EXPERIMENTAL PROCEDURE

A total of 32 different samples were taken at four different locations. The locations of the sites are shown in Figure 1 and the sampling schedule in Figure 2. City site A was on the roof of the six-story oceanography building at the Florida State University at maximum distance from the outlet of a ventilation system. City site B was on the roof of the Tallahassee central fire station, situated on the steep slope of a hill, so that the sampler was only 100 meters away and at about the same level as the intersection of two major streets in the city. No ventilation outlets were on the roof, but employees in the fire station use the roof as a parking lot. Forest site F was near ground



Figure 1.
Locations of sampling
sites.

level deep in Apalachicola National Forest at a place known as Pope Still Tower, accessible by a sand trail in the midst of pine trees and some 10 km from the nearest road. On the coast, site X is a rooftop location at the two-story FSU Marine Laboratory, site Y on a rural sandy beach, and site Z a two-story roof location near an oil and gas fired electric power plant in the small village of St. Marks. The samplers were placed on a table during all sampling at a height of about 1 meter above the ground or the roof.

The sampler was a 5 stage cascade impactor, purchased from Delron, Inc., Columbus, Ohio, with a single orifice per stage and a flow rate of 1 liter per minute. Flow rates were regulated by a critical flow orifice and checked before and after each run. Typically, about 3 m^3 of air were sampled during a 48-hour run. Aerodynamic "cutoff" diameters for the impactor stages were given by the manufacturer as: stage 1, $4 \mu\text{m}$; stage 2, $2 \mu\text{m}$; stage 3, $1 \mu\text{m}$;

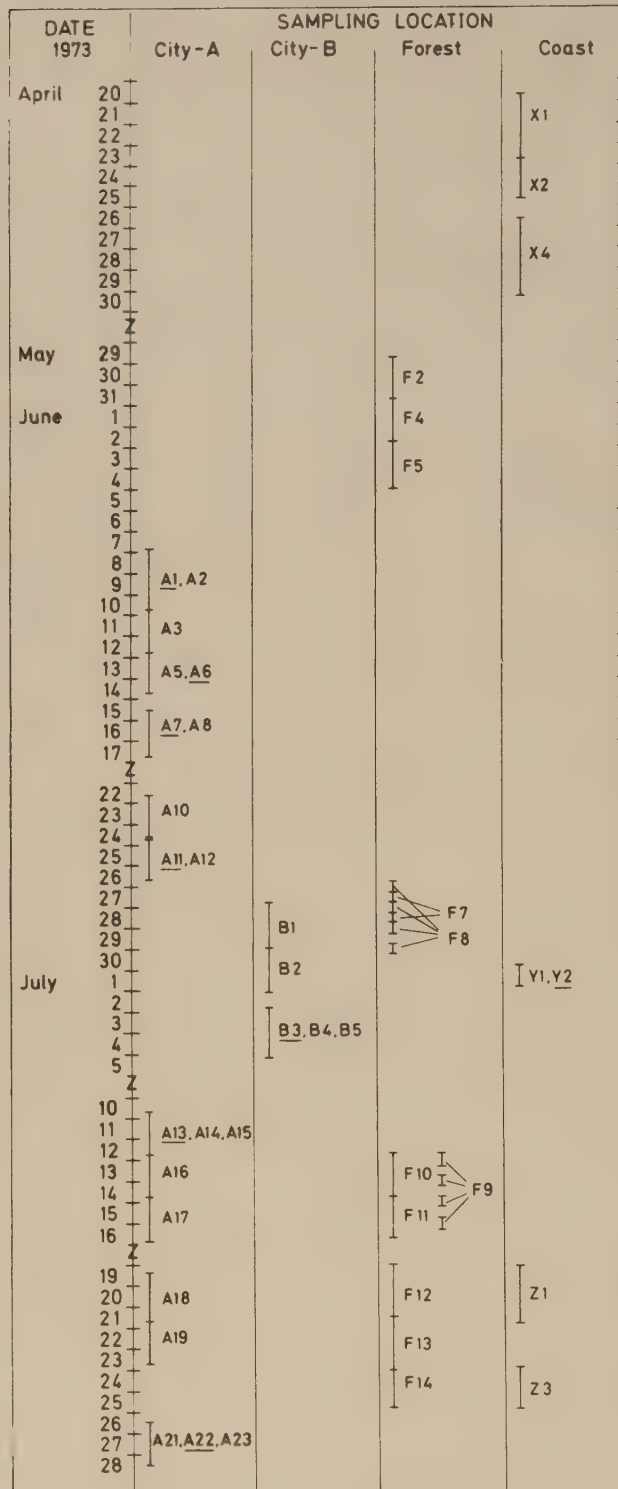


Figure 2. Sampling schedule.

stage 4, $0.5\ \mu\text{m}$; stage 5, $0.25\ \mu\text{m}$. In some of the impactor runs, backup filters were used to collect particles of diameter less than $0.25\ \mu\text{m}$.

The circular glass impaction slides were previously coated with a thin polystyrene film from benzene solution and were made sticky by evaporation of a thin layer of paraffin. After sampling, the foils were transferred by floating on water to specially designed aluminum frames for subsequent irradiation in the FSU Super FN Tandem Accelerator. The samples were analyzed by PIXE for up to 14 elements from S to Br by K X-ray measurement and for Pb by L X-rays. An irradiation lasted for 10 - 15 minutes and the X-ray spectrum was recorded with a Si(Li) detector and stored on magnetic tape for subsequent evaluation. The use of protons in the MeV range, 3.7 MeV in this experiment, together with thin samples on thin supporting substrates permits multielement analysis at or below the nanogram level. Also, by special design of the irradiation chamber, non-homogeneous samples such as impactor deposits can be analyzed. The quantitative results are obtained by a simple calculation from physical constants and irradiation parameters, and standards are used only to check the performance of the system.

Although the method is basically very specific, some elements near the limit of detection are sometimes difficult to identify unambiguously from small X-ray peaks in the absence of secondary peaks. In aerosol analysis, this problem arises mainly in a few impactor stage 5 analyses, where weak peaks may occur at $\sim 4.50\ \text{keV}$, the energy of TiK_{α} and BaL_{α} . Ba was never detected in other samples from this study, and consequently these weak peaks have been handled as if they were Ti peaks. The whole analytical procedure has been carefully evaluated, and the results are published separately (Johansson et al., 1974a).

Elemental abundances in individual impactor runs showed smooth variations with particle size, indicating an excellent degree of performance of both the sampling equipment and the analytical procedure. In some runs where a backup filter was used, large particle elements such as Fe were found only in negligible amounts, indicating good particle retention by sticking to the impaction stages. During some of the runs, duplicate samples were taken to evaluate the performance of the procedure, and the results for elements not near their detection limits indicate a total error of 20 - 30 %. Detailed

accounts of these reproducibility experiments are given in a separate publication (Van Grieken et al., 1974).

RESULTS AND DISCUSSION

The sampling strategy adopted for this study was chosen to reveal basic relationships among the detected elements in the aerosol. North Florida provides a good natural setting for such an investigation as only a few strong sources are expected to be operating: sea, soil, forest, and only a modest amount of pollution, since large industrial centers are located several hundred kilometers away, the area has a low population density, and Tallahassee has no large industries of its own.

Fe was detected in all samples. S, K, Ca, Ti and Zn were found in almost all samples, while Cl, Mn, Cu, Pb and Br were frequently detected. Cr, V and Ni were present in some samples. Size distribution trends were generally smooth and consistently similar. Certain exceptions were observed which would be related to local meteorological conditions during sampling.

Figure 3 shows, i.a., the averaged concentration data for Fe. Several interesting observations may be made from the graph. The coast locations consistently yield lower Fe concentrations, as would be expected if Fe has no major source in the direction of the sea. The concentrations at the two city sites are close to each other for all particle sizes. For the forest site, however, concentrations are similar to the city for stages 2 to 5, while stage 1 shows a significantly lower value at the forest site. This deviation will be discussed later.

Particles in the atmosphere can be considered to originate by two types of mechanisms. Small particles ($\lesssim 1 \mu\text{m}$) may result mainly from condensation of material volatilized, e.g. during combustion or a natural process. Large particles ($\gtrsim 1 \mu\text{m}$) may predominantly result from dispersion, e.g. by mechanical abrasion or erosion, and may be emitted into the atmosphere by industrial activities, wind action on soils, sea spray, etc.

Examination of size distribution data therefore indicates possible source characteristics for the various elements detected. In this study, Fe was found mainly on large particles, suggesting a source of dispersion type.

Cl, K, Ca, Ti, Cr and Mn also showed large particle preference while S, Br and Pb appeared predominantly on small particles. For V, Cu and Zn rather similar concentrations were found in each of the particle size ranges, possibly because of the additive effect of several sources.

Absolute concentrations of the elements obtained in single measurements may be strongly influenced by meteorological conditions. It is therefore useful to normalize elemental concentrations to that of an element with presumably one predominant source. By comparing the ratios obtained with corresponding numbers for anticipated sources, geochemical insights may be found. Constancy of an interelement ratio over all particle sizes points to a common source for the elements compared while deviations, perhaps limited to a certain size range, suggest additional sources to be operating for these particle sizes or fractionation effects associated with particles from the source considered.

In preparing Figures 3-5, Fe has been assumed to be derived mainly from soil (Egorov et al., 1970) and the ratios to Fe are compared with corresponding ratios for the elements in average soil. The assumption of a sole terrestrial source for Fe is corroborated by evidence published separately (Johansson et al., 1974b) where subsets of the data for mainly marine air flow and mainly continental air flow were compared. Pb is assumed to have a dominating terrestrial pollution source and the Pb/Fe ratios, although decreasing markedly with increasing particle size, were independent of "marine" or "continental" air flow during sampling, suggesting a terrestrial source also for Fe. Analytically, Fe usually gives strong X-ray peaks and is easily determined with little interference or X-ray absorption problems, thus minimizing the uncertainty introduced by the normalization procedure.

Titanium coheres with Fe in most samples and the ratio is remarkably constant and close to the geochemical average of the ratio of these elements in soils. This suggests strongly a source of soil composition for these elements. For the smallest particles, there is an indication of elevated ratios that might arise from an additional source of small particle Ti.

Large particle Mn shows a very constant ratio to Fe, independent of sampling location. The closeness of the measured ratio to that of these

Figs. 3-5. Average concentrations of Fe and weight ratios for other elements to Fe plotted versus impactor stage number, equivalent to a logarithmic scale of aerodynamic particle diameter. The vertical bars represent one standard deviation of the mean of the data set. The numbers at the bottom of each graph show the number of real values included in the averages. Where this number is less than the corresponding number of samples analyzed in Table 1, the element was below detection limit in the remaining analyses. If the element was detected in more than half the number of analyses, a value has been plotted; otherwise an upper limit value is indicated. The soil ratios are calculated from Vinogradov (1959). Points for city site A are open circles (o), city site B are closed circles (●), forest are open squares (□), and coast are crosses (x).

Table 1
Numbers of Samples Included in This Study

Number of Impactor Samples	City Sites		Forest Site F	Coast sites X, Y, Z
	A	B		
Taken ^a	12	3	* 11	6
Analyzed ^b				
Stage 5	12	2	9	5
" 4	12	3	11	6
" 3	10	3	11	5
" 2	12	3	10	5
" 1	12	3	8	5

a. Numbers represent separate samplings of the atmosphere. An additional 12 samples were taken simultaneously with some of those listed as tests of reproducibility of sampling and analysis procedures.

b. During handling a few samples were lost due to breakage of unusually thin polystyrene foils.

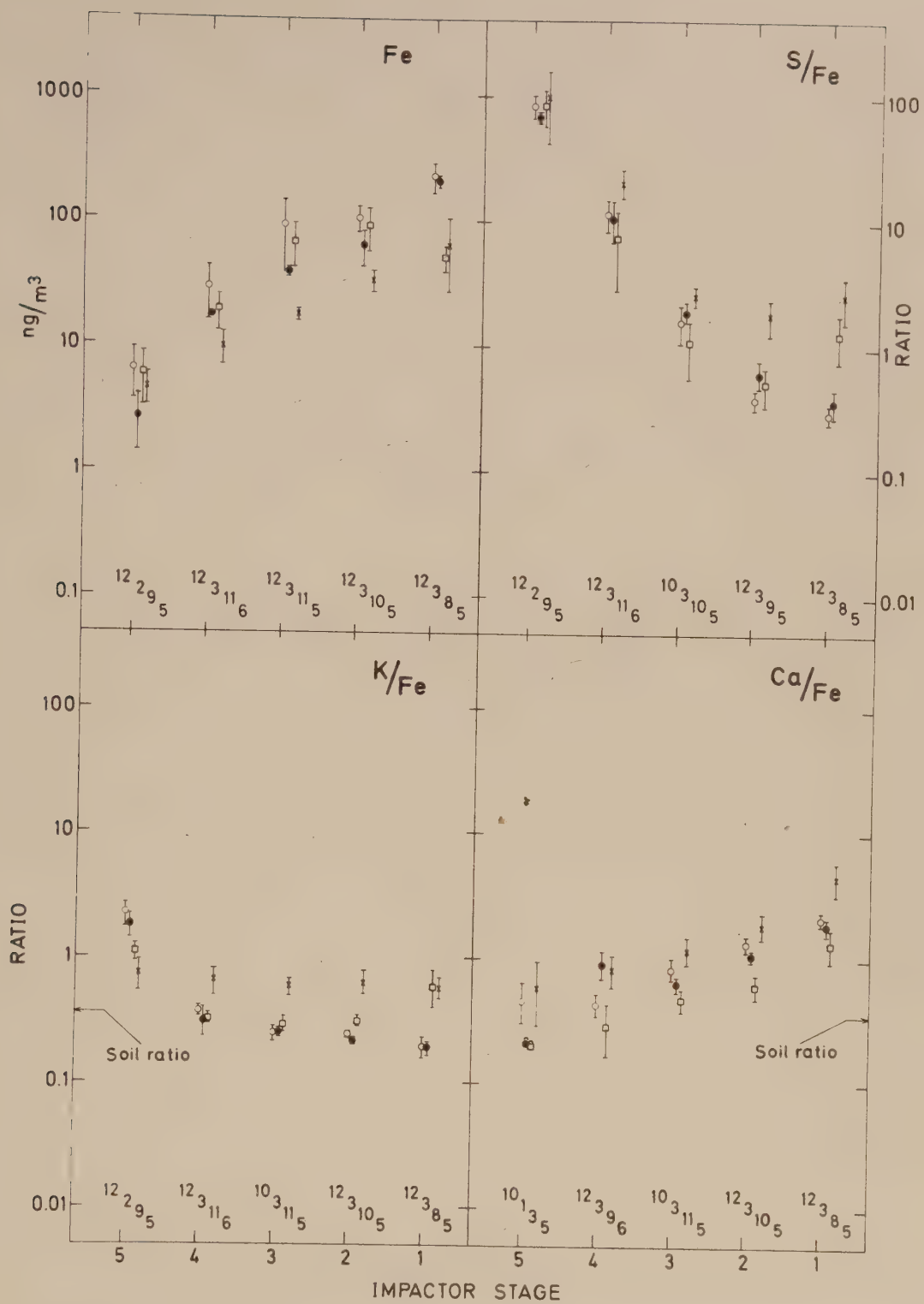


Figure 3.



Figure 4.

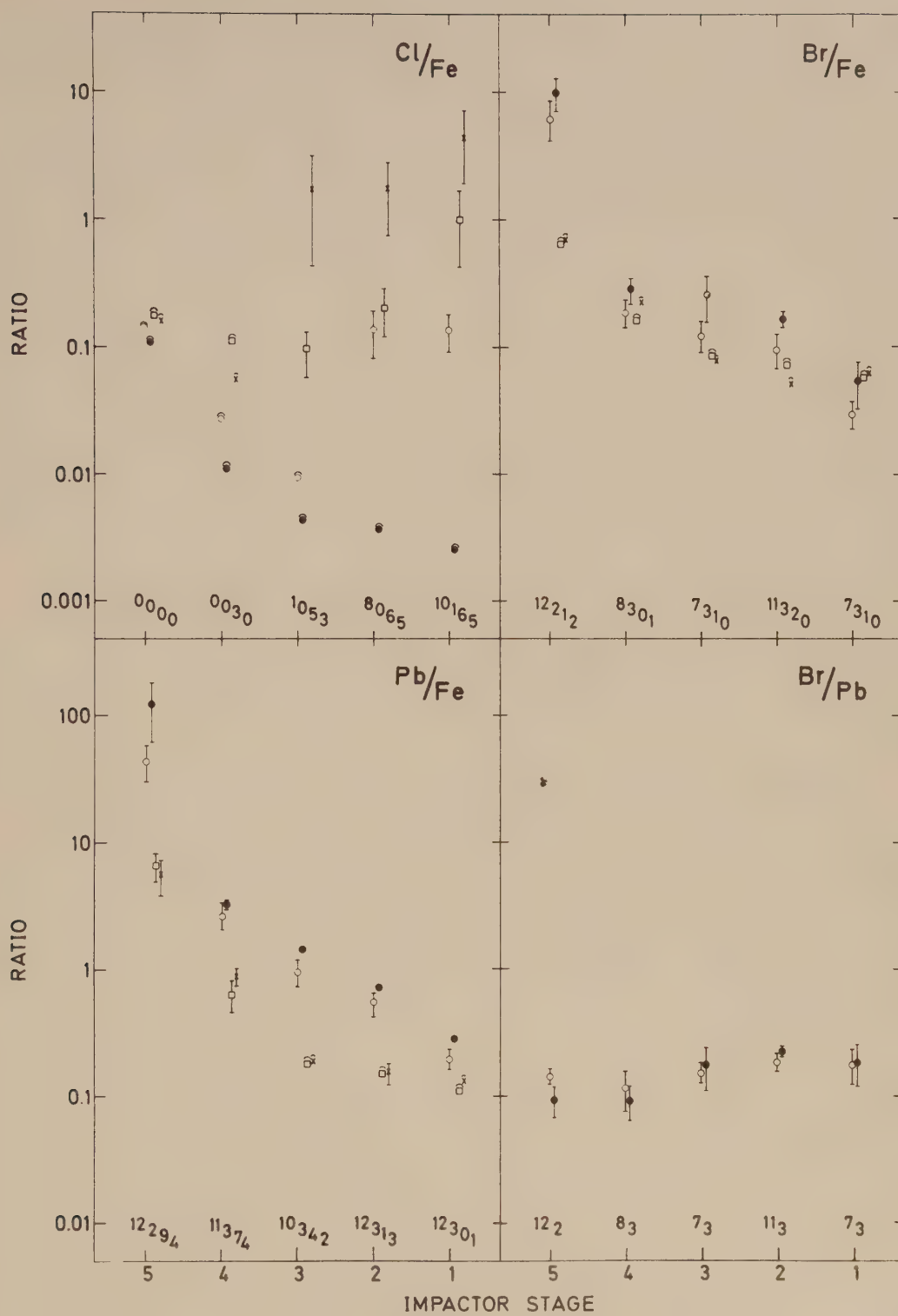


Figure 5.

elements in average soils points to a common source for large particles.

Calcium, another dispersion element, shows ratios to Fe close to that found in soils for small particles, while coarser particles are significantly enriched in Ca at all sites. Several sources for large particle Ca are indicated in addition to average soil: the high values in the coast samples suggest a sea source while the values obtained at the inland sites may result from the dispersion of limestone, which is abundant in North Florida. Further sampling will be needed to establish the relative strengths of these sources.

Potassium appears to belong to the group of soil derived elements although the size distributions show some additional features. The coast samples show K enrichment on medium and large particle sizes, possibly by K in sea spray particles. Stage 5 values for the other sites are significantly elevated indicating a terrestrial regional source for small particle K.

Chlorine is strongly large particle oriented and appears only on the first impaction stages. It also shows rapidly decreasing values as the distance to the coast increases, consistent with sea spray being the principal source for Cl.

Sulfur is markedly small particle oriented relative to Fe. There is no variation in the S/Fe ratios with geographical location of the sampler for stages 3-5 indicating that no strong small particle sulfur source is localized in Tallahassee. Thus S apparently has a natural regional source or results from long range transport of sulfur from outside the region. The coast samples show additional S on the coarsest particles, suggesting a sea source for some of this sulfur.

Some elements, such as Zn, Cu, Sb and Se have been found to be strongly enriched in the atmospheric aerosol relative to soil composition from measurements in remote locations (Rahn, 1971) and from urban studies (John et al., 1973); Bogen, (1973). Recently, Zoller et al. (1974) found similar enrichments at the South Pole. The sources of these elements acting to produce these enrichments have not yet been identified. In our study, when Zn and Cu were detected, both showed strong regional enrichments relative to soil composition when compared with Fe. (The very high stage

1 Zn/Fe value at the forest site is possibly local contamination from a nearby tower of galvanized iron.) The greater ratios to Fe for smaller particle sizes suggest that vapor-to-particle processes are operating. The Cu enrichment has been suspected to be contamination from vacuum pumps in some reports. In this study, the pumps were of a sealed type and precautions were taken during sampling to vent the exhaust far from the sampler, making contamination from them less likely. Abrasion of automobile tires, which has been suggested as a source of airborne Zn, is probably not important in Tallahassee since the Zn/Fe ratio is not elevated at our city sites compared to the rural sites.

As indicated earlier, the comparison of Tallahassee aerosol, sampled from rooftop locations, with rural forest aerosol, sampled near ground, showed a significant difference for stage 1 concentrations of Fe. The plots of Ti and Mn ratios to Fe reveal no similar difference and the excess Tallahassee large aerosol particle component contains these three elements in soil ratios. Possibly, surface dust recycling in the city, induced by man's activities, may contribute to the total particulate load. It would appear that, in any city, diurnal variation in stage 1 particulate matter may well be ascribed to diurnal variations in anthropogenic stirring activity as well as to industrial cycles. Consequently, size distribution information is required to handle this possibility when interpreting the results of multistation monitoring data in terms of source strengths.

In spite of the proximity to the sea, Br does not follow the Cl size distribution and Br/Cl ratios are much above the corresponding value for sea water. Apparently, essentially all Br is derived from automotive pollution from leaded gasoline and the marine source is relatively insignificant.

The Pb/Fe ratios show a marked difference between the city sites and the rural sites, as expected if Pb is purely an automotive pollution component. Br/Pb ratios are about 0.1 - 0.25 on all stages. This is in agreement with ratios reported by Martens et al. (1973) from the San Francisco Bay area but below the value 0.39 in gasoline, assumed to be the major source for both Br and Pb. Robbins and Snitz (1972) suggested a model with a rapid initial loss of Br from the particles by volatilization at the

surface of a particle. The initial loss should then be followed by a diffusion rate controlled volatilization. If their model is valid, smaller particles would show lower Br/Pb values as they have large surface to volume ratio. Our results qualitatively tend to support the approach of Robbins and Snitz, although the spread in the data is too high to make a definitive statement.

Size distributions from dispersion processes seem to be quite variable and may prove to be an important tool in identifying sources and their strengths. The stage 1 cutoff of the impactor used in this study gives little resolution in this region, and it is felt that an additional stage for the largest particles should be used in future investigations. A suitable backup filter or the use of low pressure impactors for the smallest particles would be desirable for further evaluation of the interesting small particle effects reported here.

CONCLUSIONS

A proton accelerator is a novel instrument in aerosol analysis. The optimum choice of accelerator delivers small beams (μA) of protons with a few MeV energy with, compared to requirements in nuclear physics, very low demands on beam quality. Accelerators nowadays are stable machines routinely operating around the clock with only modest shut-down times for maintenance. As there are hundreds of them available in many countries, the use of an accelerator represents no great difficulty or cost. The results of this model study demonstrate the usefulness of the instrument for investigating sophisticated problems in atmospheric chemistry as well as for similar analytical problems in other research fields.

Means of the size variation trends for different elements were distinctively different suggesting aerosol subpopulations of differing mineralogy and chemical properties. Interelement ratios and their variation with particle size exhibited considerable constancy over all samples taken, suggesting for the elements measured in this study that localized sources are of less importance to aerosol composition than are area sources or long range transport over the region from remote sources.

The results of this study demonstrate the value of a detailed investigation of a natural environment and its relationships as a prerequisite to subsequent research on more complex atmospheric environments that may have been altered by man's activities.

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